MANUAL AND AUTOMATED MEASUREMENT OF THE CHEMICAL OXYGEN DEMAND (COD.) OF WASTEWATERS

by

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A THESIS SUBMITTED FOR THE DEGREE OF

MASTER OF SCIENCE

AT THE

UNIVERSITY OF ASTON IN BIRMINGHAM

MAY 1973.

SUMMARY

The problem of water pollution in the United Kingdom and the usefulness of oxygen demand tests to measure the organic pollution is outlined. Because oxygen demand tests are arbitary the relative merits and shortcomings of the commonly used tests are discussed, as are some new techniques for measuring organic pollution. The correlation between the results of the different tests is examined and is shown to be very limited. An historical review of tests based on dichromate oxidation shows that many different procedures have been proposed, but that an almost universally accepted procedure now seems to have evolved.

Automation of the procedurs is shown to be possible but the difficulties in doing so are stressed, in particular the problem of the time parameter. A twofold requirement for an automated COD. system is outlined. Experiments with a commercial continuous flow system showed it to be unsuitable for the both requirements. Work with a hybrid part discrete, part continuous flow system is described. Some useful information was gained but the system proved unreliable for monitoring purposes. A completely discrete system was finally developed. A laboratory version for discrete samples and a version for monitoring sewage works final effluent have both been extensively used. The development and performance of both systems is described. The analytical precision and comparative agreement using different analytical parameters is reported.

It is suggested that the COD. test is becoming increasingly important and is widely applicable across the whole spectrum of water pollution technology. The future of automated COD. procedures

is seen as one of wider acceptance and further development. The manual procedure could possibly benefit from further investigation, and some preliminary work and suggestions for further investigations are included.

IMPORTANT NOTE.

The term COD. at one time referred to any oxidation demand test using any chemical oxidising agent. More recently the term has come to mean oxygen demand tests where potassium dichromate is employed as the oxidising agent. This is certainly the case in America and acceptance of the term in this sense is becoming widespread. To avoid any ambiguity the term COD. in this thesis refers exclusively to oxygen demand tests using potassium dichromate as the oxidising agent.

ACKNOWLEDGEMENTS.

The author wishes to express his gratitude to the members of the Upper Tame Main Drainage Authority and to Dr. N. Harkness, Chemist to the Authority, for permission to publish the details of the work in this thesis.

In addition I would like to express my appreciation to the following for:-

Dr. E. R. Clark of the Department of Chemistry, The University of Aston in Birmingham, for his help and guidance.

Mr. D. G. Willetts for providing OCV. : COD. data and details on the updating and future design modifications of the COD. system.

The staff of the Minworth, and Works and Rivers laboratories of the U.T.M.D.A. for performance details and analytical data during routine use of the two COD. systems.

Mrs. D. L. Smith for typing the thesis.

Mrs. S. Smith for preparing the photographs and diagrams.

Miss D. Williams for invaluable help in preparing the final copy.

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CHAPTER I.

INTRODUCTION

1.1. THE PROBLEM OF WASTEWATER.

The estimated volume of water used in 1968 in England and Wales was 5,000 million gallons per day (MGD) which is equivalent to 23 million cubic metres per day (M^3/D) of which some 3,100 MGD (14.1 million M^3/D) was discharged to sewers for treatment at sewage disposal works. (1). This was made up of about 1,800 MGD (8.0 million M^3/D) of domestic sewage and about 1,500 MGD (6.8 million M^3/D) used by industry. This averaged about 60 gallons per head of population.

In 1970 the amount of effluent being discharged to rivers and canals was estimated as 4,000 MGD (18.4 million M^3/D) (2) and consisted of sewage effluent, crude sewage, industrial effluent and underground mine waters. This volume represents a discharge of about 83 gallons per head of population.

It has been forecast that by the end of the century water usage will have doubled and the volume requiring treatment will also have doubled. (3).

Readily accessible sources of water are now almost fully utilized. About one third of the present supply comes directly from rivers which will certainly be extracted to a much greater extent as increased demand stretches the existing resources. Some 90% of sewage works effluent in England and Wales is discharged into rivers or estuaries and the remainder direct into the sea. It follows that there already exists a significant proportion of sewage effluent in the rivers. Some rivers in heavily populated industrial centres already contain a higher percentage of sewage effluent than raw water and many rivers at present extracted or which may require to be extracted for potable

supplies already have a significant level of sewage effluent present. Obviously any increased abstraction of river water will make it increasingly difficult to maintain existing water supply standards without a substantial increase in the quality of discharged effluents.

1.1.1. Organic pollution in domestic sewage can be reasonably forecast and be expected to be of a fairly consistent nature and level. Pollution by trade effluent is often extremely variable with respect to both quality and quantity. A reasonable figure for the percentage trade effluent flow in the total overall flow to a works can be estimated over a period of time. However, over short periods of time it can and will fluctuate widely as will its quality. The effect of trade effluent is therefore much more damaging to the treatment plant because of shock loading than would be the case if either a steady flow or pollution load could be maintained. The presence of industrial effluent will always influence both the nature and strength of a sewage. The overall average for industrial effluent in total sewage flow for the United Kingdom is about 50% but will vary widely for different sewage works. It is the presence of these wastes which normally cause the greatest problem in the treatment of sewage. Industrial effluents can be broadly classified into four groups: (4).

A) Effluents from food and drink manufacture.

B) Other organic effluents arising from industries using natural products, animal or vegetable.
e.g. wood, leather and wool industries.

C) Engineering industries which discharge effluents with metals, cyanides, etc.

D) Chemical effluents arising from chemical industry or industries utilising chemicals.

Effluents in the first two classes contain pollution which is

usually mainly organic in nature. The third class of effluent is not normally organic in nature but often degreasants, emulsifiers and oil, both soluble and insoluble, are present which constitute a significant organic pollution load. Effluents of the fourth class can be extremely diverse in nature. Some may contain chemicals which are relatively low with regard to organic load but which can, by the nature of the compounds, be extremely toxic.

Among other possible sources of organic pollution, not covered by the industrial effluents listed and normal domestic effluent, can be included farm effluents and accidental spillages arising from industrial or road accidents where spillage is swilled into the nearest drainage connection or water course. Wilful or accidental discharge of oil for example is now an increasingly common occurence.

1.2. EFFECTS OF ORGANIC POLLUTION.

The effect of pollution is governed by the extent or degree of pollution. Many of the older sewage disposal works receive flows and/or levels of organic matter way above their design capacity producing an overload factor and in consequence discharge effluents of unsatisfactory quality.

Rivers and other watercourses are affected by the quality of discharged effluents. In its natural state a river supports fish life, plant life and other animal life in a stable ecological system. Pollution will disturb this system and normally the main effect will be due to organic content of discharged effluents.

Slight pollution by discharged effluents will cause little harm to a river as the normal self-purification system of a river can nullify the organic pollution. Unfortunately this self-purification which is mainly biological is limited. (5). The

volume of water extracted, combined with increasing discharge of effluents considerably reduces the percentage of raw water in many of our watercourses. This overreaching of the self-purification level has the effect of impairing and eventually completely destroying the natural ecological pattern, and will produce either an unnaturally balanced system or a completely dead river.

1.2.1. The effects of organic pollution in rivers stems mainly from the fact that much of it is biologically oxidisable and therefore acts as demand on the dissolved oxygen present in the river water. If the demand is too great the bacterial decomposition of the organic compounds will continue in the absence of oxygen, not aerobically as with normal self-purification, but anaerobically. This results in production of a range of foul smelling breakdown products from the organic compounds plus sulphides formed by a reduction of sulphate.

The extent of the effect of organic matter on a river caused by oxygen depletion depends not only on the amount added but to an equal extent on the physical characteristics of the river. The re-oxygenation of the river occurs much more rapidly in a turbulent, shallow, fast flowing river than with a placid, deep, slow moving river. Most rivers in the United Kingdom are of the latter type.

Allowance must be made, when determining the effects of organic pollution, for the organic content of the suspended solids present in discharged wastewater. A large proportion of the insoluble organic matter will soon settle to the bottom of a slow moving watercourse within a short distance of its discharge point. This will concentrate a good deal of the organic content of a discharge within a relatively small area intensifying the rate of deoxygenation over this zone to a much higher extent than would

the soluble organic component of the discharge. This concentrated deoxygenation over relatively small areas is one of the worst feature of organic pollution. It is intensified when storm water conditions cause a substantial increase in the river velocity. The increase in flow has a scouring effect on the sedimented organic solids, causing them to become suspended. Large areas of the river can rapidy become deoxygenated by the action of the suspended organic solids which move down the river associated with large slugs of deoxygenated water producing a devastating effect on the aquatic life of the watercourse.

The actual extent of the effect of the organic pollution is difficult to define and will become increasingly more so due to the complications introduced by the present of other, mainly inorganic, pollutants. The ecologically stable balance of animal and plant life in a stream is seriously jeopardised by, for example, non-ferrous metals and ammonia present in many sewage effluents. The relationship between the degree of organic pollution and the distribution of animal and plant life, therefore, can be defined only with a good deal of caution. That it will have a major effect however, is undoubted.

1.3. CHEMICAL OXIDATION AS A NON SPECIFIC MEASURE OF OXYGEN DEMAND.

Any oxidation demand test must, when used to analyse a sample of unknown composition, give a purely arbitary result dependent on the parameters of the test. That is unless the oxidising conditions are such that even the most difficult to oxidise compounds will be decomposed. The severity of the oxidising conditions vary widely between the commonly accepted standard procedures. They are all to some extent arbitary.

1.3.1. The COD. test could be objected to from the point that it is a 'blanket' test covering both biodegradable and the non-

biodegradable compounds. (6). The river system can, assuming sufficient oxygen present, break the biodegradable compounds down to a relatively stable odour free, harmless end product. The non-biodegradable type of compound will have no such oxygen demand upon the river system. However, non-oxidisable organic compounds will possibly impair the water quality from the point of colour, taste, odour and fish toxicity simply because they are not removed biologically. It is also difficult to predict if any particular compound is entirely resistant to bacterial attack. This is particularly applicable to solid organic matter. Whereas stable soluble organic pollution is carried away to sea, the solid organics often settle to the bottom and very slowly degrade, usually anaerobically possibly forming soluble, more easily degradable compounds. Such grounds for dismissing the relevance of the COD. test are therefore not sufficiently objective.

1.4. RELATIONSHIP OF BIOCHEMICAL AND CHEMICAL OXYGEN DEMAND.

Basically oxygen demand of wastewater is measurable in two ways. Biologically by measuring the amount of oxygen uptake or depletion in a standardised system due to the ability of bacteria present to biologically oxidise both soluble and insoluble organic waste present in the sample. Almost universally biological oxidation is synonymous with the BOD. (Biochemical Oxygen Demand) test. Chemical oxidation demand measures the amount of a chemical oxidising agent used to oxidise any substance(s) present in the wastewater, whether organic or inorganic, capable of being oxidised by that reagent under a stated set of conditions.

The two approaches are not truly comparable as regards to the results given when considered overall but can be related within certain narrow fields or for certain types of wastewater. For instance, the sewage or final effluent from a specific sewage

disposal works or a specific factory waste may be fairly consistent in character and would give a reliable COD. : BOD. relationship. There is however a fundamental difference in the concept of the two tests, as well as a number of important factors which makes a universal correlation for all wastewaters an impossibility.

1.4.1. The chemical test is considerably faster than any biological test and completed in a matter of hours as against several days for a biochemical oxidation.

1.4.2. Chemical oxidation conditions are considerably more severe than biochemical oxidation conditions and therefore the oxidation proceeds much nearer the complete oxidation of the oxidisable compounds in the sample. It is possible for both systems to achieve complete oxidation or for neither to complete the oxidation. However, quite a high percentage of the time the COD. test will completely or nearly completely oxidise the oxidisable compounds, whereas the BOD. test will rarely achieve completion using the normal 5 day incubation period.

1.4.3. The chemical tests are not normally subject to inhibiting factors. The biological oxidation will be inhibiting partially or completely by anything present in the sample, dilution water or apparatus which is biologically toxic.

1.4.4. The chemical test is non-specific and will oxidise organic matter, both biologically inert and degradable, also any inorganic matter capable of being oxidised by the particular oxidising agent used. Ammonia or organic nitrogen do not exert an oxidation demand with wet chemical oxidation methods. Biological oxidation is considerably more limited normally only measuring the amount of oxidation required to stabilise the biologically oxidisable carbonaceous organic waste. However, under certain conditions oxidation of nitrogenous compounds will occur to a variable extent

in the standard BOD. test.

1.5. THE PRE-EMINENCE OF THE BOD. TEST.

The biochemical oxidation demand test has a long uninterrupted history with regard to the testing of wastewaters.

The test was first described in 1868 (7) and apart from a modification in the standard incubation temperature, plus some accepted modifications to allow for abnormal samples, the test remains basically as it was originally proposed by the Royal Commission on sewage disposal. (8). The test in its present day form (9, 10) is universally accepted and applied wherever waste water testing is practiced. This is one of the greatest values of the test. It is the major sewage strength criteria used for the design of sewage disposal plants.

1.5.1. The emergence and growing importance of a chemical oxidation demand test can be put down to the shortcomings of the BOD. test. Many of these shortcomings are related to the standard parameters of the test. Often the BOD. test is either too slow or is unsuitable for use with the sample under test.

1.5.2. There is no intention in this thesis of suggesting that a chemical oxidation demand test should entirely replace the traditional BOD. test. Rather that in many cases one test will supplement the other. However, in many cases a chemical oxidation demand value is a satisfying alternative to a BOD. value. Oldham (11), in a paper on oxidation values, concludes that whilst the permanganate value (PV.) test has not a great deal of merit the COD. test has a good deal to recommend it as a procedure for determining oxidation demand strengths for charging purposes and also for measuring sewage works efficiencies. Other workers (12, 13, 14) have commented favourably on the COD. test as a procedure for measuring

the oxygen demand strengths of a variety of samples.

1.5.3. The BOD. test is likely to continue for a considerable time as a standard procuedure in its present form. The position regarding chemical oxidation procedures is much more fluid. At present it appears that dichromate is widely accepted as the most suitable oxidising agent and various contries have now accepted either a tentative or a standard chemical oxidation procedure based on potassium dichromate as the oxidant.

CHAPTER 2

A REVIEW OF OXYGEN DEMAND TESTS AND A DISCUSSION ON POSSIBLE CORRELATION BETWEEN RESULTS.

2.1. BIOCHEMICAL OXYGEN DEMAND (BOD).

This test was originally described by Frankland in the report of the Rivers Pollution Commission of 1868. (7). The Royal Commission on sewage disposal later proposed as a standard that the weight of dissolved oxygen required by a definite volume of sample for the process of biochemical oxidation during 5 days at 65°F be a measure of the purity of the sample. (8). The test was designed to simulate natural conditions in a river where bacteria in the presence of oxygen utilises organic matter as food causing it to break down into simpler organic and inorganic compounds. It is important to note that the BOD. test was originally intended only to measure the effect of waste discharges on river waters. Other bacteria also utilize oxygen to break down nitrogenous organic compounds via ammonia into nitrite and/or nitrate. The present day BOD. test can be defined as the amount of oxygen consumed by the sample, by microbiological and chemical action, when incubated at 20°C for 5 days. It is normally expressed as the milligrams of dissolved oxygen consumed per litre of sample.

In practice the sample is diluted with well oxygenated clean water to which has been added certain nutrients K, Na, P, Cl, Ca, Fe and Mg required by the living organisms. The dissolved oxygen content of the diluted sample is determined before and after a 5 day incubation stage either titrimetrically by the Winkler (15) procedure or alternatively using a dissolved oxygen probe. Ideally the dilution should be such that half the dissolved oxygen originally present is utilised. This is frequently difficult to achieve in practice.

The BOD. test has a number of advantages and disadvantages. It is the most commonly used test for sewage strength and has been over the past few decades. Its use as the measure of sewage strength will have been used as the criteria in nearly every sewage plant ever designed. Its longevity, universal standardisation and acceptibility makes the test extremely useful as a method of comparing waste waters either historically or geographically. The BOD. test was for a long time the only test able to give a rough indication of the organic load of a wastewater on a river or watercourse that is biologically degradable. Both Tebbut (14) and Oldham (11). however, question the validity of the BOD. test as an idicator for sewage works practice. Arguing that the relatively large rapid substrate removal by adsorption follows by oxidation in the presence of high concentrations of micro organisms and ample oxygen, found in a sewage works, is in no way represented by the single stage bottle incubation, in the dark, using a limited supply of micro organisms and oxygen.

2.1.1. The test has a number of limitations and Weston (16). lists at least eighteen different variables which could influence the result. The BOD. tests main drawbacks are the time required for the test to be completed, the interference from toxic substances and its non-specificity. The 5 days incubation period is a serious time lag particulary with respect to works control but is unavoidable because of the nature of the test. Even this extensive period is really too short as the ultimate BOD. often requires about 20 days to reach near completion. Susceptibility to toxic substance is probably the worst drawback of the test where the origins of samples are very diverse and underlines the point that the BOD. test was originally designed only as an approximation to the conditions to be expected for a

river. There are many substances which could interfere with the biological process without being detected. A busy routine laboratory dealing with wastewaters from a variety of sources, sewage works, rivers, trade premises, storm waters, abnormal discharge at treatment plants could unknowingly attempt to analyse biologically toxic samples. It is probable that many erroneous results due to inhibition have been recorded. That this is so does not imply criticism of the laboratory concerned. Because to anticipate or detect inhibition, expecially when it is not total, requires a combination of intuition and experience backed up by an extensive amount of extra analyses which still may not indicate the extent of inhibition.

Although the strength of a watewater discharge as measured by the standard BOD. test is almost universally used by river authorities as a criteria of its acceptability for discharge, the variable response to organic and ammoniacal nitrogen casts doubts to its validity for such a purpose. It is a recognised fact that the carbonaceous BOD. of partially nitrified effluents from activated sludge treatment works are invariably enhanced to a variable extent, up to as much as a factor of 10, due to the residual ammoniacal nitrogen in the sample being oxidised. Of equal concern is the large difference in results produced by taking different aliquots of such samples. The larger the aliquot the greater the amount of nitrifying bacteria in the incubation bottle which in turn will cause greater ammonia oxidation. Therefore it is easily possible for a good effluent in a state of incipient nitrification to have a much higher BOD. than a much poorer quality effluent in which no nitrification has occured.

The BOD. test is enhanced if inorganic reducing agents

capable of being oxidised by molecularly dissolved oxygen, such as sulphite, sulphide and ferrous iron, are present. They will have an immediate initial dissolved oxygen demand and they will only be included when the BOD result is based on the calculated initial dissolved oxygen not on the initial dissolved oxygen measured after a short period of standing. In samples where, due to the absence of bacteria, initial seeding with bacteria is necessary the seed source can have a considerable bearing on the BOD. results due to the question of bacteria acclimatisation.

2.1.2. There is no standard against which the accuracy of the test can be measured. A glucose/glutamic acid solution however can be used to run a check on the reagents used and the technique of the analyst. The figure achieved being required to lie within defined limits. Ballinger (17). has shown that the expected standard variation of the BOD. test is about $\pm$ 20% of the mean value.

There has been published a large number of modifications of the BOD. test intended to overcome known interferences with the standard procedure. Most of the more significant procedures are included in standard methods publications. (9, 10). Probably the two most widely used modifications procedures are that of Alsterberg (18)., who included sodium azide in the reagents used for determining the dissolved oxygen, to eliminate the effect of nitrite ion (NO_2^-) commonly encountered in sewage works wastewaters. The second modification (19) uses allyl thiourea (ATU). to inhibit the nitrification of ammonia so giving a BOD. figure attributable to carbonaceous oxidation only. This modification is being increasingly run as a routine test in addition to the standard BOD. test in many of the larger wastewater laboratories.

2.2. THE PERMANGANATE VALUE. (PV).

The permanganate value (PV). is also sometimes referred to as the oxygen absorbed value (OA). This test is a chemical oxygen demand test and can be defined as the amount of oxygen absorbed by a sample from a sulphuric acid solution of potassium permanganate under a standard set of conditions. The parameters normally defined are the strengths of the acid and potassium permanganate present in the solution and the temperature and time of the reaction.

There is no universal standard procedure but there are only a few basic procedures in common use. The test mostly used in Britain (9) specifies a concentration of N/80 potassium permanganate in the mixture which is incubated for 4 hours at 27°C. Originally, the temperature of incubation was 80°F (26.7°C) but was later fixed at exactly 27°C. After incubation the residual potassium permanganate is determined by addition of excess potassium iodide and titration of the liberated iodine with N/80 sodium thiosulphate. It was quite common to use N/8 permanganate solution for testing trade effluents. The use of the stronger permanganate tends to give higher oxygen demand results than the N/80 permanganate by a factor of about 1.6. A frequently used variation of the PV. test is the three minute PV. test which requires the solution to be titrated three minutes after the permanganate addition. This procedure measures the immediate oxygen demand of the sample and can give a useful guide to the type of sample. It is obviously important, because of the variable results possible using different modifications to define the parameters used when reporting PV. results. (13).

The measurement of water quality using potassium permanganate was described as long ago as 1893 by Wyatt (20). and the PV.

test is the oldest chemical oxidation demand test now in use. Analytically, the test is simple and requires little skill to produce results in a short period of time. It also has the added advantage of allowing a lot of samples to be processed simultaneously with a relatively small amount of apparatus. The permanganate value is normally quoted as milligrams of oxygen, donated by the permanganate, required to oxidise 1 litre of sample. As it is purely a chemical test it cannot be expected to yield the same information as a purely biological test, nor be affected by agents capable of inhibiting biological agents. The permanganate value is, however, of questionable value because the amount of organic matter in a sample oxidised by acid potassium permanganate will vary considerably dependent on the organic compounds present in the sample. Different organic compounds will be oxidised to totally different extents. For example, neither acetone nor toluene are oxidised by acid potassium permanganate whereas phenol is about 80% oxidised. Nitrogenous matter is not oxidised by acid potassium permanganate.

Published procedures normally stress that for many samples the permanganate value is dependent on the sample aliquot taken. Because of this it has long been accepted that roughly one half of the permanganate added should be consumed in the test. It has been stated that it is acceptable if the amount consumed lies between one and two thirds the amount of permanganate added. Simpson (13) has shown that such a wide latitute can lead to imprecise results and that PV. results found when half the permanganate is consumed are not the maximum values obtainable.

2.2.1. Various modifications of the permanganate value test have been reported using higher temperatures, to speed the reaction, and much shorter heating periods (21, 22). in an attempt to produce

quicker, more accurate and reproducible results. If the permanganate value must be adhered to, there is much to commend this approach.

Because of the antiquity of the test there is a great deal of old analytical data available. Unfortunately much of it is of doubtful value because the analytical parameters used are not known.

It is interesting to see that since the 9th edition (21). no subsequent editions of the American standard methods manual included a permanganate value. On the other hand the latest British standard methods book (9). has retained the test.

2.3. THE CHEMICAL OXIDATION DEMAND TEST (COD).

The dichromate value test has now become widely known as the chemical oxygen demand test (COD), despite this term being originally a general term covering any test, using a chemical oxidising reagent, to measure the amount of oxygen uptake by a sample. The procedure most widely used (10). consists of refluxing, under a condenser, a mixture of sample plus a standard volume of dichromate to which has been added sufficient sulphuric acid to make the final solution 50% v/v sulphuric acid. After refluxing for 2 hours, the residual dichromate is determined by back titration with standard iron (II) ammonium sulphate solution. The COD. value is normally quoted in milligrams of oxygen, donated by the dichromate reagent, required by one litre of sample. It is possible to shorten the refluxing period if the sample is known to oxidise easily, but this would be unwise with most samples of waste waters which are of unknown composition. Analytically the test is more precise than the BOD. and PV. test with considerably greater reproducibility than either of these

tests. Ballinger (17) found that between different laboratories the COD. test has a precision of about ± 8% of the accepted COD. value. This is a reasonable level of accuracy between different laboratories, and would almost certainly be even more precise for duplication carried out by the same laboratory. The apparatus required for the test and the test procedure are both comparitively simple. It is therefore relatively easy to set up and operate sufficient apparatus to carry out a large number of COD. determinations per day, should a continuing demand for the test exist. The COD. method is now receiving a good deal of acceptance as a procedure for determining oxidation values. A good many research papers now quote oxidation demand values as COD. values, both with and without other types of oxidation demand measurement. Accurate COD. values can be obtained for many chemicals by analysing pure samples. The oxygen demand determined by this test represents the demand of the organic matter in the sample plus any matter capable of reducing potassium dichromate such as sulphite and iron (II). Neither organic nitrogen or ammoniacal nitrogen are oxidised in the test. Carbonaceous matter may not always be completely oxidised and the extent of the oxidation is normally dependent on the chemical structure of the organic compound. It has however considerable advantages over the permanganate value as a chemical oxidation test particularly with regard to reproducibility and the extent of oxidation with nearly all organic compounds. Reasonable agreement with theoretical COD. values can be obtained for most organic compound by analysis of pure samples. Because the COD. usually approaches the ultimate carbonaceous oxygen demand of a waste water it is capable of producing meaningful data, especially

when taken in conjunction with other data. For instance, it is easy to accurately determine ammoniacal and organic nitrogen and estimate their oxygen demand separately. It is therefore possible to suitably modify the empirical formula proposed by McGowan (23). to yield an ultimate oxygen demand (UOD.) value. (11). UOD. = Oxygen demand as determined by COD. test + 4.5 (ammoniacal nitrogen + organic nitrogen). One of the shortcomings of the COD. method is said to be its lack of sensitivity. The American procedure (10). shows good sensitivity for most purposes down to a level of 50 mg/l but is less accurate for still lower levels. However, Moore and Walker (24). have shown by suitable choice of reagents that accurate results in the order of 10 mg/l can be obtained. Despite this, there is reluctance by some authorities analysing waters with low COD. levels to use this test, on the grounds of accuracy. The American standard procedure also incorporates the use of silver as a catalyst and mercury to eliminate chloride interference. There are a number of modifications to this widely adopted procedure which are of some importance. These modifications fall into four categories.

2.3.1. First is the procedure using stronger sulphuric acid concentrations in the reflux mixture. A recently issued British Standard Institute (B.S.1) method (25). and the now superseded British recommended procedure (26). both specify a ratio of sulphuric acid to total aqueous content of 1.2 : 1 (54.5% v/v sulphuric acid), as against the American procedure which used a 1 : 1 ratio (50% v/v H_2SO_4). This is a very important difference because the reflux temperature with the greater acid level is about 11°C higher. This imposes more

severe oxidising conditions and the oxidation of 'difficult to oxidise' substances should proceed further. With most samples oxidation goes almost to completion with either procedure. Increased oxidation by high temperature is referred to by Weber, (27). who determined the organic carbon value of samples by complete oxidation of carbon to CO_2 using dichromate/sulphuric acid sample digestion. Complete oxidation of all organic compounds, including heterocyclics, is claimed by Bleier (28). by heating the sample with a dichromate/sulphuric acid digestion mixture at 170°C. The mixture was pumped through a glass coil, which gave about 11 minutes retention period, held in an oil heating bath. The mixture is about 80% v/v sulphuric acid to prevent boiling. Most automated procedures use a heating temperature below the reflux temperature of the acid mixture.

2.3.2. The second modification uses a shortened heating period which is frequently allied to the higher temperature. It would seem reasonable to expect that a shorter reaction time using higher temperatures, could produce equivalent oxidation to a longer heating period using a lower temperature. Both Jeris (29). and Madison (30). used this principle in proposed manual procedures requiring only a minimal heating period once the mixture reached fuming and 165°C respectively. Most automated wet chemical systems discussed later use the higher temperature plus short heating period technique. A 2 hour reaction period is not possible if a reasonable throughput of samples is required.

2.3.3. A third modification important to routine analysis is the scaling down of the standard procedures to semi-micro scale analysis. This was first described by Jenkins et.al.(31). who used a scaled down version of the British standard procedure to routinely analyse large numbers of samples. A similar scaled

down procedure was later adopted by the Water Pollution Research Laboratory based on the American standard procedure. The most recent British standard procedure (9). recommends the scaled down version of the American standard procedure. A scaled down procedure is specified by the Upper Tame Main Drainage Authority, Birmingham, as the prescribed method for analysis of trade effluents for the purposes of fixing the trade effluent treatment charge. Larger volumes than those used by Jenkins are employed as well as the sulphuric acid : aqueous solution of the American standard procedure. This modification, which is described in the appendix, anticipated the new British standard procedure coming into line with the acid concentration used in the American procedure. This procedure replaced the Jenkins procedure formerly specified by the Authority.

2.3.4. The fourth important modification of the COD. method is the automation of the manual technique.

2.4. SOME OTHER OXYGEN DEMAND AND RELATED MEASUREMENTS.

There are newer, less widely practiced techniques for determining organic loading of waste water. The two best known are the organic carbon value (OCV) and respirometry. Both tests require equipment not normally encountered in a small wastewater laboratory which has hindered any possible large scale adoption of these techniques.

2.4.1. Organic carbon value (OCV) is the estimation, in milligrams per litre of organic carbon in the sample. This test is based on the oxidation of the carbon to carbon dioxide with subsequent determination of the amount of carbon dioxide produced. Originally, chemical wet oxidation was used (27, 31, 32). frequently by digestion with sulphuric acid/dichromate mixture and was a time consuming

procedure requiring careful supervision. More recently a rapid physico-chemical procedure has been suggested by Van Hall et.al.(33). using a combustion technique which involves introducing microlitre volumes of the sample into a heated furnace packed with a suitable oxidising catalyst, over which is streamed pure oxygen, and estimating the CO_2 produced from the organic carbon in the sample by a suitable physical procedure. A commercial version of the system is marketed by Beckman Instruments Inc., Fullerton, Calif. Modifications of the system (34, 35, 36). include a step for reducing the CO_2 to methane which is then estimated by gas chromatography. In all cases inorganic carbonates and dissolved CO_2 must be initially removed. Recently a system using a continuous sample injection into the combustion furnace instead of discrete injections by syringe has been developed by the Water Research Association. It is being commercially marketed by Phase Separation Limited, Bromborough, Cheshire.

The recently published automated analysis system of Bleier (28). is of interest as it carries out a simultaneous analysis for COD. and OCV. on the same sample aliquot. The OCV. is determined by estimating the CO_2 released during the heating of the sample with dichromate/sulphuric acid to measure the COD. of the sample. The OCV. determination is a speedy and convenient way of estimating organic pollution levels. It can be used to express the oxygen demand of the organic pollution load where a satisfactory empirical relationship between the two parameters has been established. It cannot of itself indicate organic pollution loading in terms of oxygen demand as the existing degree of oxidation of the organic carbon is not determined.

2.4.2. Attempts to follow the course of biological breakdown of

organic pollution has led to developments in the field of respirometry. The Warburg respirometer has been used for many years in biochemical oxidation studies, but suffers from a number of disadvantages mainly connected with the very limited size of the system.

Monometric instruments have been developed which overcome the limitations on sample size and the development of these systems has been reviewed by Jenkins (37). Repirometry tests can now be followed indefinitely if required being limited only by the systems capacity to absorb all the evolved CO_2. The increased size allows the added advantage of being able to withdraw sample aliquots for additional analysis.

The respirometric procedure is a dynamic system where the oxygen taken up by the sample is replaced and simultaneously the evolved carbon dioxide is absorbed. The reaction is monitored by measuring the amount of replacement oxygen fed into the system against time. Therefore, the cummulative oxygen supplied plotted against time can give the rate of the reaction and indicate time lags. Montgomery et.al.(38, 39). have published useful reviews on the subject of respirometry, covering the techniques and apparatus now available. Simpson (13). strongly advocates the use of respirometry for assessing the strength and treatability of trade wastes. Respirometry is an excellent tool for use in researching problems arising from treatment of trade wastes and other problems associated with sewage treatment. As a method of determining the strength of waste waters it is too complex to use for routine analysis of large numbers of samples. More over, as Oldham (11). points out, in a sewage treatment works removal of organic matter by bioflocculation is a rapid process. This is followed by the much slower biochemical

degradation which is the process followed by oxygen uptake measurements. Therefore, respirometer measurements obscure the actual pattern of substrate removal. This can, fortunately, be followed by utilising the COD. of shaken and filtered samples (40, 41).

2.5. AUTOMATION OF OXYGEN DEMAND PROCEDURES.

All the methods mentioned, were devised as manual procedures for use in a laboratory by skilled technicians. Automated versions of some of the procedures are often desirable both for laboratory and monitoring purposes. Because of the particular nature of oxygen demand tests the only approach seems to be to use an automated version of the manual procedure, when results comparable with the manual test are required. Any hope of using some new technique seems rather remote because of the rather arbitary nature of the tests. Automated procedures for many of the tests mentioned in this chapter have been published. Basically, the biggest snag has been the time factor involved. The BOD. test is the prime example because the use of a 5 day incubation period in the manual process seems insurmountable when it comes to automation. No one has seriously suggested an automated procedure. There may be some hope for the future, however, in the work of Updike and Hicks (42), who described experiments with what could be described as a form of specific ion electrode for measuring biodegradable organic matter. Both the PV. and COD. procedures have been automated by a number of workers. The procedures are mostly automated wet chemical tests, though some physical-chemical techniques are often incorporated as part of the analytical system. These procedures have approached the question of the time factor by treating the two parameters of

time and temperature as interchangeable correlated factors. This assumes that the set time and temperature parameters of the standard manual procedures can be duplicated by shortening the time and increasing the temperature of the reaction. There is strong evidence to show that this is true for any one compound or sample. It seems unlikely that there is any one alternative set of temperature/time factors which will universally apply to equal the standard method parameters. Despite this it has been found possible to apply a set of new conditions to a variety of samples and be confident that the results are in reasonable agreement with the results found by the manual procedure.

2.5.1. Henriksen (43). has published an automated PV. procedure using the well known Technicon auto-analysis equipment and gives results to indicate good agreement with the manual procedure. Unpublished work by Hey (44). shows that an automated technique is capable of giving excellent agreement with standard manual procedure results. Unfortunately, different heating temperatures suited different types of samples. The two most suitable temperatures using heating periods of 20 minutes were 60°C and 65°C. At the lower temperature crude samples such as sewage and settled sewage gave the best agreement with the manual results. The partly purified waste waters such as humus tank feeds and effluents, grass plot effluents and river waters tended to give low automated results because much of the easily oxidisable material had been removed. At the higher temperature these partially purified samples gave better agreement with the manual procedure than the crude samples, which gave high automated results because of the stronger oxidising conditions. One other drawback emerged because of the solids in the samples. It is normal to use shaken samples for the manual analysis which employs a

titrimetric finish. However, both the automated procedures mentioned used a colorimetric end point. Solids taken as part of the sample caused unintentional spikes on the recorder graph as they passed through the colorimeter flow cell.

2.5.2. A number of automated COD. test systems have been described, most being automated versions of the manual procedure. However, Stenger and Van Hall (45). have described an intrumental system using CO_2 as the oxidant. The CO_2 oxidises the organic carbon in a furnace to carbon monoxide being in the process reduced itself to carbon monoxide. The carbon monoxide produced is measured by infra red spectroscopy.

$$CO_2 + C \text{ (from organic pollution)} = 2CO$$

Complete oxidation is achieved and the authors refer to the measurement as the CO_uD. (ultimate COD.) and claim very good agreement with conventional COD. results for sedimented sewage. Good agreement will only be possible when the conventional COD. test gives complete or nearly complete oxidation. Additionally nitrogen compounds produce an oxygen demand using the system and chloride interferes in the test.

2.6. CORRELATION OF THE RESULTS GIVEN BY VARIOUS OXYGEN DEMAND AND RELATED TESTS.

2.6.1. The relationship meriting most attention has been that between COD. and BOD.

There can be no an priori intrinsic relationship between the two parameters but many workers have attempted to establish one and have concluded that limited correlation can and does exist. (11, 12, 31, 46, 47, 48). Though some evidence regarding relationships between specific trade effluents does exist (11). most of the

investigations have been connected with sewage works samples and watercourses receiving sewage effluents.

The best agreement between the independent findings of various workers is for raw domestic sewage. There is general agreement that the COD. : BOD. ratio lies between 1:0.45 and 1:0.50. It is possible the variation above or below these ratios could well be due to a waste having a particular characteristic conferred by the presence of trade effluent whether industrial or agricultural. Abnormal ratios of BOD. : COD. are frequent in relatively small rural works receiving volumes of less than about 200,000 gallons per day (900 cubic metres per day). Often this is connected with agricultural waste and/or abnormally high suspended solids. Shock loading of larger sewage works is buffered by the greater dilution factor. Wells (47). gives a conversion factor for raw domestic sewage of BOD. = (COD x 0.48) - 20. This cannot be universally applicable but it is possible to determine a relatively reliable factor experimentally for any particular Works. This should be periodically checked in case the nature of the sewage has changed.

Few figures are quoted for a ratio for sewage after primary sedimentation (settled sewage) which should, however, yield reliable ratio factors for most sewage works and will not be complicated by abnormal high solids. Any abnormally high solids in the raw sewage will be evened out in the sedimentation process. Jenkins (31). gives figures for COD. : BOD. ratios of crude sewage of some Birmingham, England sewage works which vary between 1:0.31 and 1:0.52. Oldham (11). quotes typical figures of 1:0.55, while Eden (49). gives a value of 1:1.44 which can be converted to a COD. : BOD. ratio of 1:0.50. Annual averages for the year 1971-72 for 12 large sewage works in the Upper Tame Main Drainage Authority's area showed COD. : BOD. ratios for

shaken raw sewage samples ranged from 1:0.24, to 1:0.45; with an overall average of 1:0.34. 3 of the works had ratios less than 1:0.3 and all three had high average suspended solids. Only 1 works had a ratio higher than 1:0.40. The ratios for settled sewage for the same period at these works ranged from 1:0.30 to 1:0.41 with an overall average of 1:0.36. These figures show that variability can often result from variable suspended solids. The ratios are somewhat lower than the ratios quoted previously and this may be due to the large trade effluent content in the sewage for most of the works quoted.

The correlation between BOD. and COD. for samples after biological treatment is much poorer. Figures ranging between a COD. : BOD. ratio of 1:0.1 and 1:0.3 have been found by some of the works previously quoted. However, the picture is not that complicated and can be seen to be governed by a number of factors. Firstly, the large drop in the ratio after biological treatment is caused by a considerable removal of the biodegradable compounds, leaving a considerably higher percentage of the compounds only oxidisable by chemical means. It seems obvious that the better the final effluent the lower the COD. : BOD. ratio. Oldham (11). states that with about a 90% BOD. removal the factor is about 1:0.25 but that with a greater than 90% removal the factor abruptly drops to about 1:0.1. The ratio is closely linked with the amount of suspended solid present which in turn is dependent upon whether a works effluent received tertiary treatment. Practical experience shows that effluents, from sewage works providing only primary and secondary treatment, containing in the range 15 to 45 mg/l solids will have a COD. : BOD. ratio of about 1:0.25. However, for effluents receiving tertiary treatment and secondary effluents with very low suspended solids of less than about 10

milligrams per litre the ratio will be about 1:0.1. Figures published by Jenkins (31). and by Oldham (11). from a number of sources tend to confirm this view. It would be useful to have consistent BOD. suspended solids and COD. suspended solids ratios to predict the effect of the suspended solids on these two parameters and their ratio. Oldham has computed ratios of BOD:SS and COD:SS of 1:4 and 1:0.83 using published figures from a very limited number of sources. Personal experience, from as yet only a limited amount of experimental work indicates that these ratios are nearer 1:2.5 for BOD:SS and 1:1.3 for COD:SS. Figures from Painter et.al.(50). and Truesdale and Birbeck (51). tend to confirm these ratios. Incipient nitrification in a final effluent can produce enhanced BOD's which make nonsence of these quoted ratios. Using the BOD. found using the allyl thiourea modification to suppress nitrification, normally confirms the ratios quoted.

It is contentious whether to quote soluble oxidation demand values on settled, filtered or centrifuged samples should this information be required additional to the normal total demand figures normally quoted. It makes little difference with most final effluents which technique is used as these samples are usually well clarified. There is a considerable difference shown in the results for raw and settled sewage because of the colloidal nature of much of the solid matter. The question also arises as to what filter media to use when filtering. It is personal opinion that only glass fibre papers should be used. Acid washed cellulose papers have been used for the purpose and while seemingly suitable for use with filtered BOD. analysis they have been suspected of causing some erroneous soluble COD. and OCV. results.

Table 1 gives the soluble COD. values for samples using the different techniques. Individual analysts will have to decide which system provides results of most value to themselves.

As a collorary the author is also analysing the suspended solids in various types of solids to try and establish typical BOD. and COD. values. Known aliquots of samples are filtered through thoroughly washed, weighed Whatman GF/7 glass fibre filter papers which retain 1 micron size particles. The papers are washed, dried and weighed to determine the amount of solid matter. The filter paper plus solids are then placed in the BOD. bottle or COD. flask and the determination completed. A well washed, unused paper is used to give a blank value. This work is part of a long term study though preliminary results indicate some definite correlations do exist.

TABLE 1

SOLUBLE COD. VALUES USING DIFFERENT TECHNIQUES FOR SOLIDS REMOVAL

SAMPLE	SOLUBLE COD. IN MILLIGRAMS PER LITRE		
	SETTLED	FILTERED	CENTRIFUGED
Crude Sewage	252	130	138
Crude Sewage	589	232	331
Crude Sewage	315	195	220
Crude Sewage	458	288	344
Final Effluent	52	55	78
Final Effluent	98	94	90
Final Effluent	30	34	24

2.5.2. The organic carbon value (OCV.) has a theoretical ratio of 1:2.6 with the COD. value. In practise this is modified by other elements being subject to chemical oxidation and the organic carbon present already being partially oxidised. The ratio normally found for a wide range of samples of all types is 1:3.0 $\pm$ 0.5. Compounds strongly resistant to oxidation will differ considerably but it does apply for most domestic waste waters. OCV:COD relationships for industrial waste waters must be carefully qualified. Ford (52). quotes figures varying from 1:1.75 for a type plant waste to 1:6.60 for a chemical plant waste containing sulphides and thiosulphate. Many of the chemical wastes quoted do come in the range 1:3.0 $\pm$ 0.5. The figures given by the same worker for chemical waste waters after biological treatment are significant. The ratio OCV. : COD. of the raw waters having high ratios dropped by a factor of at least 50% in all the examples quoted, after biological treatment. This would indicate either most of the material oxidised chemically is also biochemically oxidised, that the carbonaceous compounds, although oxidised, remain in the waste water as partially degraded products. Alternatively volatile organic and/or inorganic compounds which exert a large COD demand have been air stripped from solution.

2.7. EXTENT OF OXIDATION

Table 2 shows the percentage oxidations based on the theoretical value for a range of pure compounds taken from results published by a number of workers.

TABLE 2

THE COD. VALUE FOR SOME PURE COMPOUNDS AS A PERCENTAGE OF THE THEORETICAL VALUE.

REFERENCE	1.	2.	3.	4.	5.	6.	7.
Glucose	99.7	96.4		100		94	94.6
Starch	95.0						
Cellulose				97			
Pyridine	0	1.2		0			
Acetone		96.4	92.2				
Ethanol		95.4	96	43	92.7		
Lactic Acid							
Acetic Acid	94	98.4	93.5	2	95.1	93.9	
Oleic Acid		95.0					
Stearic Acid			95.0				
Glycine	42	99.4		32			
Toluene			60				
Benzene		42					
Alkyl Benzene Sulphonate		96	91.6				
Diphenyl Guanidine			101.6				97
Alanine					80.6	45	
Furoic Acid					97.6		
Ortho Cresol					95.8		
Phenol			96				
Hexanol						94.2	
Butyric Acid						91.3	
Glutamic Acid						80	97.3
Piconilic Acid							12.3
Sucrose							97
Phthalic Acid							98
Sodium Stearate							84

1) Taken from Jeris. (29).
Note: Oxidation of glycine nitrogen is assumed.

2) Taken from Dobbs and Williams. (53).
Note: Oxidation of nitrogen in glycine is ignored.

3) Taken from Wilson. (54).

4) Taken from Moore, Kroner and Ruckhoft. (55).
Note: No addition of Ag^{+} catalyst resulting in low results of Ethanol and Acetic Acid. Also oxidation of glycine nitrogen is assumed.

5) Taken from Moore and Ruckhoft. (12).

6) Taken from Moore and Walker. (24).
Note: Using oxidation with weak Potassium Dichromate (0.05N and 0.025N).

7) Taken from Jenkins et.al. (31).

Table 2 shows that many organic compounds will be almost completely oxidised by the standard COD. procedures. Oxidation of nitrogen whether as part of the compound under test or as ammonia does not occur. Some classes of compounds are resistant to oxidation to varying degrees by the standard manual procedures. Heterocyclic compounds are very resistant to oxidation while compounds possessing aromatic benzene rings in their structure also show resistance to oxidation. The benzene ring is only partly oxidised but as most side chain substituted groups are readily oxidised the overall percentage oxidation varies accordingly. Side chains in heterocyclic compounds are similarly easily oxidised.

Table 3 gives a randon selection of typical results for the crude sewage feed and final effluents from two pilot scale activated sludge experimental units. Samples are frequently analysed for a wide range of parameters including soluble and total COD. and OCV.

The table shows that the raw sewage shows very consistent ratios for both values. The consistency is much poorer for the final effluents which is possibly indicative of analytical inconsistency at low values. However the average ratios do show consistency and the sort of figure expected.

TABLE 3

OCV. : COD. RATIOS FOR RAW AND TREATED SEWAGE WORKS SAMPLES.

SAMPLE	OCV. IN MILLIGRAMS PER LITRE		COD IN MILLIGRAMS PER LITRE		OCV:COD. RATIO	
	TOTAL	SOLUBLE	TOTAL	SOLUBLE	TOTAL	SOLUBLE
CRUDE SEWAGE	114	59	645	148	1:5.5	1:2.5
	149	81	500	195	1:3.3	1:2.4
	220	83	915	220	1:3.3	1:2.7
	219	108	820	300	1:3.7	1:2.8
	135	74	500	214	1:3.7	1:2.9
	157	98	625	272	1:3.9	1:2.8
	136	77	550	230	1:4.0	1:2.6
	190	116	665	230	1:3.5	1:2.0
	119	77	460	204	1:3.9	1:2.6
	144	87	523	239	1:3.7	1:2.6
AVERAGE					1:3.9	1:2.6
FINAL EFFLUENT Pilot Plant No. 1.	34	24	74	44	1:2.2	1:1.3
	31	28	74	64	1:2.4	1:2.3
	27	18	57	40	1:2.1	1:2.2
	27	18	54	44	1:2.0	1:2.4
	30	16	114	74	1:3.8	1:4.6
	36	24	134	80	1:3.7	1:3.3
	28	22	62	42	1:2.2	1:1.9
	24	20	79	60	1:3.3	1:3.0
	26	18	90	50	1:3.5	1:2.8
	37	26	93	84	1:2.5	1:3.2
AVERAGE					1:2.7	1:2.8
FINAL EFFLUENT Pilot Plant No. 2.	26	12	65	49	1:2.5	1:2.4
	24	16	41	30	1:1.7	1:1.9
	27	23	50	40	1:1.9	1:1.7
	28	24	114	85	1:4.1	1:3.5
	37	31	114	87	1:3.1	1:2.8
	26	25	67	50	1:2.6	1:2.0
	26	23	85	70	1:3.3	1:3.0
	21	21	75	55	1:3.6	1:2.6
	30	22	85	68	1:2.8	1:2.3
	23	19	79	38	1:3.3	1:2.0
AVERAGE					1:2.9	1:2.5

CHAPTER 3

HISTORICAL REVIEW OF THE COD. TEST

3.1. ORIGINS OF CHEMICAL OXIDATION DEMAND PROCEDURES

Since the inception of a biological oxidation demand test by Frankland in 1870 (7). and Dupre in 1882 (56). there have been numerous other oxidation tests published in the literature. The majority of these tests have been based on chemical oxidising agents of which only four have received serious consideration, these being potassium permanganate, potassium dichromate, ceric sulphate and iodic acid.

Potassium permanganate became the most widely used oxidising agent and for many years the only recommended or standard chemical oxidation procedures were based on permanganate. (9, 21, 22, 26, 57). That permanganate procedures have never been very satisfactory is evidenced by numerous other proposed modifications. (58, 59, 60, 61, 62).

Because of the unsatisfactory performance of permanganate renewed interest in the use of other oxidising agents resulted. In 1914 Klein (48). compared permanganate, ceric sulphate and dichromate as reagents for the testing of sewage strength. He found that ceric sulphate gave only 60-70% of the value given by dichromate, but two or three time the values given by permanganate. In 1951 workers at the environmental Health Centre, Ohio, published a report (64) on a comparative study of a number of proposed chemical oxidation demand tests. The tests included several procedures

based on dichromate, (30, 55, 65). an iodic acid procedure (66). and the standard PV. test. (21). They concluded the dichromate test of Moore et.al. (55) was to be preferred on the basis of accuracy, reproductability, ease of manipulation and range of applicability. On the basis of this work the procedure was adopted as the American Standard Method. (10).

3.2. POTASSIUM DICHROMATE AS AN OXIDISING AGENT.

Adeney and Dawson (67) were among the first to use dichromate oxidation in a form recognisable with present day standard procedures. Their procedure used a one hour reflux of the sample, acidified with sufficient sulphuric acid to give a 33% v/v sulphuric acid content. They also included a step for the elimination of chloride interference. A modification to this procedure was published by Muers (68) in 1936, which is almost identical with the American standard procedure. The procedure differed in using a one hour reflux instead of the present two hours reflux, and did not include the use of mercury to suppress chloride interference. Muers found the Adeney and Dawson procedure gave low results for effluents from the cheese making industries due to the short chain acids and alcohols present. He found almost quantitative oxidation could be obtained by increasing the sulphuric acid level to 50% v/v and incorporating silver sulphate as a catalyst. Residual dichromate was estimated by back titration, with thiosulphate, of the iodine released by addition of potassium iodide to the refluxed mixture. This estimation of dichromate was quicker but less accurate than Adeney's procedure of using iron(II) sulphate with an external indicator. Muers specifically noted that 50% v/v sulphuric acid

was nearing the maximum possible as there was a measurable loss of oxygen due to dichromate decomposition when the solution was refluxed. He also noted that although low chloride levels could be tolerated, high levels caused serious interference.

There seemed to be little sustained interest in the use of potassium dichromate for oxidation demand measurement in Britain following the work of Muers. In 1941 Klein (48). published a comparison of different procedures for determining sewage strength. He used the rather long, complicated dichromate procedure suggested by Abbott (69) in preference to the simpler procedure of Muers.

The next interest in the use of dichromate appeared to be the publication in 1946 by Rhame (70) of another modification involving the use of dichromate. Rhame's results tended to be erratic because the mixed digestant/aqueaus sample required to be heated in an open beaker to remove the aqueous phase resulting in very variable digestion. Rhame's procedure was then modified by both Madison (30) in 1947 and Ingolls and Murray (65) in 1948. The Madison procedure depends on digesting the sample with a concentrated sulphuric acid/phosphoric acid mixture which is terminated after fuming has taken place for exactly four minutes. This test requires close supervision and is time consuming. The Ingolls and Murray procedure had the drawbacks of an unstable mixed reagent, a possible variable blank, and the use of the iodimetric procedure for measuring the dichromate. In 1949 Moore et.al. (55) published their procedure which was eventually selected as the preferred procedure by United States public health service workers (64).

The procedure advocated by Moore et.al. was remarkably similar to the procedure of Muers without these workers apparently being aware of this work. They encountered the limited oxidation of

short chain acids, alcohols and hydrocarbons without being able to overcome the problem. It was not until later that the silver catalyst addition specified by Muers was belatedly acknowledged. (64)

3.2.1. The widespread use of the procedure was hampered by the interference caused by the presence of chloride. Because the interference is normally quantitative, it is possible, knowing the chloride content, to allow for the interference. One British recommended procedure (26) includes a modification allowing for chloride interference. Unfortunatly, in the presence of ammonia and amines a cyclic reation involving the intermediate formation of chloramines occurs. The chloride is oxidised to chlorine which instead of being lost into the atmosphere is trapped as chloramine to be again reoxidised. A many times enhanced value over the normal quantitative interference is therefore possible. An important b breakthrough came with the procedure proposed by addition of mercury(II)sulphate. Complete elimination of chloride interference is claimed. But the term effective suppression is more correct. There is strong evidence to show that there is still a measurable though small enhancement when chloride is present in the sample. This is due to a slight dissociation of the largely undissociated mercuric chloride complex. This dissociation is increased by the presence of silver ions which form a slightly more soluble complex. Factors worked out by Cripps and Jenkins (71) show that the interference with most samples is insignificant and could be ignored experimentally. However, they showed for highly saline samples such as sea water and salt pickling effluents that a correct chloride factor is important, especially where the

sample possess's a low COD. value. It is shown that silver ions should be omitted unless the analysis specifically requires them, because the correction factor is considerably higher when both silver and mercury are present than when the mercury salt alone has been used.

Since the introduction of the use of mercury(II) sulphate there has been no major modifications incorporated in the present day American Standard Method (10).

3.3. EXISTING MODIFICATIONS TO THE AMERICAN STANDARD PROCEDURE

There seems to be no available explanation why two widely used British procedures (26, 31.) had adopted a sulphuric acid concentration in the reflux mixture of 54.5% v/v when the existing American Standard Method specified a 50% v/v sulphuric acid mixture. Besides using this higher acid concentration, Jenkins (31) also introduced the concept of a semi micro version of the procedure including the use of silver and mercury(II) sulphate. Scaling down of the procedure is now widely practised and has big advantages with regard to cost and space saving but requires greater analytical expertise.

Jeris (29) has described a 'rapid' manual procedure which has received a good deal of interest and has received a somewhat limited evaluation by Wells (47). The procedure involves heating a mixed sample sulphuric acid/dichromate mixture until the temperature reaches $165 \pm 1^{\circ}C$ then rapidly cooling the solution, dilutiong and titrating the residual dichromate. It is emphasised that the procedure is intended to give a rapid figure for a limited number of samples and is not projected as a substitute for the standard procedure.

3.4. STANDARD PROCEDURES.

The use of different sulphuric acid concentrations was previously the only significant difference between the American Standard Method (10) and the recommended British procedure (26) updated by Jenkins (31). This has now been eliminated by the adoption of a 1:1 (50% v/v) sulphuric acid:aqueous ratio by the latest British standard procedure (9). The situation in Britain previously was confused, with an official government organisation, The Water Pollution Research Laboratory, using the American procedure but in the semi-micro form suggested by Jenkins.

The decision to alter the acid concentration to 50% v/v with a consequent change in the reflux temperature curiously parallels the change made in the British Standard BOD. procedure when the incubation temperature was raised from 65°F (18.5°C) to 20°C to conform with the practise more widely adopted throughout the world. The higher acid level would give the greater oxidation, should any difference exist between results using the two procedures on the same sample, because of its more severe oxidising conditions. It has been claimed that the higher acid concentrations produces erratic and variable blank values. In more than two years experience with the higher acid procedure running six replicate blanks daily, it has been rare to find even one of the replicates outside the accepted standard of mean daily average $\pm$ 0.1ml. It can only be concluded that erratic blanks were caused by non-uniform heating and/or poor operator technique.

3.4.1. The question of variability in results resulting from the scaling down of the procedure is sometimes raised. From personal

experience very good agreement between the macro and semi-micro techniques is achieved provided conditions and techniques are of reasonable standard. Variation outside normal experimental error will not be attributable to the method. It is a prime requisite that the heating should produce steady uniform refluxing and the apparatus be scrupulously clean. Jenkins (31) gave figures for full scale and micro scale analysis for pure substances which showed exellent agreement. The results on sewage samples was not quite as good but account should be taken of the difficulty of obtaining representative aliquots from samples containing heterogeneous suspended solids.

A recent collaborative test between five different laboratories of the Upper Tame Main Drainage Authority, Birmingham, England was carried out to test uniformity of procedure and results. The control laboratory used the macro scale procedure as given in American Standards Methods, (10) the remainder used a similar procedure scaled down with respect to volumes used by a factor of four. The apparatus used for the micro scale procedure varied slightly between the laboratories as did the mode of heating. Two laboratories used hotplates heated by town gas, one used a gas heated sand tray, one used a calor gas heated hotplate and one an electrically heated sand tray. Four samples were tested. Sample A being a solution of potassium hydrogen phthalate which is used as the COD. standard by the Authority. The other four samples were final effluents from four different sewage works ranging from exellent to poor, all possessing different levels of suspended solids. Instructions were given to carry out 10 replicates on each sample with a minimum of two blanks. Table 4. gives the average result and the range of results found for each sample by each laboratory.

TABLE 4

AN INTER LABORATORY COD VALUE COMPARISON

	POTASSIUM HYDROGEN PHTHALATE		WORKS EFFLUENT A		WORKS EFFLUENT B		WORKS EFFLUENT C	
	AVERAGE COD	MAXIMUM AND MINIMUM COD	AVERAGE COD	MAXIMUM AND MINIMUM COD	AVERAGE COD	MAXIMUM AND MINIMUM COD	AVERAGE COD	MAXIMUM AND MINIMUM COD
CONTROL LABORATORY	90	89 94	80	71 91	76	74 77	49	46 53
LABORATORY 1	94	90 97	77	74 81	80	76 83	44	38 50
LABORATORY 2	99	96 104	113	106 123	70	63 76	45	41 48
LABORATORY 3	91	90 94	73	68 79	72	71 75	41	43 47
LABORATORY 4	92	85 100	80	64 102	89	78 103	58	34 74
ATTCHATED COD SYSTEM			92	88 98	75	72 79	45	44 47

The final column gives the results found using the automated COD. system developed by this Authority. All results quoted are in milligrams per litre COD.

It was deliberate policy to choose clean samples of relatively low COD. values to test the procedure and the operator technique to the full. In the semi-micro procedure COD. values below 100 mg/l involve very small titration differences and constitute a difficult analytical test. The results indicate the scale of the test is not important, but that operator expertise is necessary and that non homogeneous organic solids in a sample constitutes a likely source of error. Poor titrimetry was mainly to blame for some poor reproducibility found by laboratory 4.

3.5. THE DEVELOPEMENT OF AUTOMATED COD. SYSTEMS.

The first automated COD. system was based on the multipurpose Technicon Autoanalyser (72) by Molof and Zaleiko. (73,74) The system is a continuous flow system based on a peristaltic pump. Separate pump tubes continuously pump sample and reagents into a mixing pot at a delivery rate fixed by the pump tube size. The mixed solution is pumped through a two-stage heated helical glass coil open to the atmosphere after which the reacted mixed solution goes through a colorimeter where the change in colour density is measured. The temperature is controlled and the retention time in the heating coil is about 20 minutes. The range of the instrument can be varied widely. Firstly by variation of sample and reagent ratios and secondly by choice of the optical wavelength used in the colorimeter. A wavelength of 440 nanometres is used to measure the decrease in the yellow $Cr_2O_7^-$ ion for low COD. ranges. Adoption of the less sensitive 600 nanometers wavelength to measure increase of the green Cr^{3+} ion

is used for samples with high COD. levels. Wagner (75) has discussed the procedure and gives results found using the Technicon system. Adelman (76) used a long helical coil in a temperature controlled oil bath at 155°C in place of the open digester heating stage. This system is the most widely used automated COD. procedure probably because the Technicon analyser is a multipurpose system adaptable for many other wet chemistry analytical procedures.

3.5.2. Bleier (28) has recently published details of an automated system for the simultaneous determination of COD. and OCV. Basically it resembles the Technicon system but includes novel modifications.

Instead of a colorimetric finish to determine the COD. value, the mixed solution after heating is treated with an excess of iron(II) ammonium sulphate and the redox potential continuously determined as an indicator of the amount of dichromate consumed. Organic carbon is determined by measuring the CO_2 released by the dichromate oxidation of the carbon with a commercial conductrometric carbon dioxide analyser. The organic carbon is related to the extent of the dichromate oxidation. It is claimed that complete oxidation of all types of organic compounds, including heterocyclic compounds, is achieved using a heating temperature of 170°C for a period of about 11 minutes. A commercial version of the system is to be marketed at some future date under the trade name Hydromat.(77)

3.5.3. The system developed by Hey et.al.(78) differs from the previous procedure in being a discrete non-continuous system based on an automated set of separate analytical sequences. The requirement for its development, actual development and assessment of its performance to date are detailed in this thesis.

3.5.4. A system commercially marketed by the Axel Johnson Institute (79) has been designed purely as an on-stream monitoring instrument. It is a large scale automated version of the manual test using a colorimetric instead of a titrimetric procedure to estimate the amount of $Cr_2O_7^{2-}$ used in oxidation. Sample and a sulphuric acid/dichromate mixture, containing dissolved silver sulphate, are metered by metering pumps to a large vessel where the solution is heated for two hours. During the heating period the optical density of the solution is monitored to measure the consumption of $Cr_2O_7^{2-}$. As a measure of the COD. value of the sample. After the two hours digestion the heating flask is automatically drained and the next sample injected, etc. Because it takes a minimum of two hours per sample analysis, the system is too slow for routine laboratory analysis purposes. The system can be modified to use much shorter heating periods if required, with a consequently greater sample throughput.

3.6. CONCLUSIONS

Prior to about 1942 dichromate oxidation demand tests were looked on and developed merely as an extension of the BOD. test. Researchers seemed mainly concerned in devising a rapid test to correlate with BOD. results.

It is only recently that the COD. has been accepted as a measurement having an intrinsic value of its own. This has resulted from the need for a much more widely applicable test to a wider range of aqueous samples than hitherto.

This acceptance has led to the interest in developing more advanced forms of the test, particularly automated versions.

CHAPTER 4

APPLICATION OF THE COD. TEST FOR POLLUTION CONTROL

4.1. ADVANTAGES OF THE COD. TEST FOR POLLUTION CONTROL.

The sewage authority laboratory can utilise the COD. test to give useful rapid information in a number of different facets of water pollution control work.

4.1.1. The rapidity of the COD. test with respect to the BOD. test, traditionally used as the strength factor in sewage works practice, makes it an attractive alternative from the works control point of view. The test requires only simple apparatus and requires less analytical expertise and actual working time than the BOD. test and is much less subject to interference. This makes it a suitable test for even poorly equipped or staffed laboratories. It is not suggested that the BOD. test should be superseded but rather supplemented. Correlation can be established for each of the sample points normally sampled for control purposes and performance information. A central laboratory serving a number of small works, without their own laboratory facilities, is able to feed back to works superintendants the COD. strength factor simultaneously with other important factors such as suspended solids levels.

The advent of automated COD. systems adds a further dimension to on-stream sewage works monitoring. The increasing automation of modern sewage and industrial purification plants calls for an increased emphasis on analytical monitoring for a range of parameters, including an organic strength factor. The alternatives are biochemical methods which are too slow. Physical methods such as optical measurement are of low specifity and cannot compute the contribution due to solid matter in the sample, and chemical methods.

At present automated chemical methods seem the most promising way of measuring an organic strength factor.

4.1.2. Analysis of trade effluents has become a major work load for many water pollution control authorities since the Public Health Act, 1961. (80) This act allowed the sewage treatment authority to recover any additional expense incurred or likely to be incurred with the reception and disposal of trade effluents. Additionally, the authority concerned is empowered to set conditions to any consent for discharge of trade effluents. Within provisions of the act an authority remains free to decide whether or not to make any charge and if a charge is made how it is to be formulated. Different policies have arisen on how to control and how to surcharge trade effluent discharges. Many authorities formulate the charging scale and the consent limits for discharges on certain parameters. An important one being the organic strength level. This is normally computed using the McGowan formula (23). for the determination of sewage strength. The organic strength factor has traditionally been based on either the PV. or the BOD. value of the trade effluent.

The use of the COD. value provides an attractive and realistic alternative to both these tests. Simpson (13), in an assessment of the technical bases for trade wastes treatment, and Oldham (11). have favourably compared the relevance of the COD. test as compared to the BOD. and PV. tests for the purpose of trade effluent charging formulae. Many industrial concerns have laboratory facilities which allows them their undoubted right to check the sewage authority's findings by employing this simple chemical test which is far easier to employ for occasional testing than the BOD. test. The City of Nottingham was possibly the first authority to use the COD. test as a basis for trade effluent treatment charging following

the work of Fearns et.al. (81).

4.1.3. It is noticeable that many recent research projects, described in the literature, requiring an organic strength parameter have favoured the COD. test. This is particularly so of work connected with the activated sludge process, where the problem of nitrification invalidates many BOD. test results and the COD. test provides a reasonable way of following the mechanics of the carbonaceous oxidation system.

4.1.4. It has not been the normal practice for River Authorities or water supply undertakings to utilise the COD. test for the assessment of water quality. One of the main arguments being the relative insensitivity of the test for clean waters which could be expected to have COD. values lower than 50 milligrams per litre down to values of 5 to 10 milligrams per litre. Moore and Walker (24). have shown it is perfectly feasible to work in this range with a reasonable degree of accuracy using weaker dichromate solutions. The weaker dichromate was shown to possess equal oxidising efficiency to the strengths normally employed. The normally employed BOD. test cannot measure the total amount of residual organic material which may be present. Figures given by various workers (12, 24). show the COD. : BOD. ratio for watercourses receiving effluent discharges. The further from the discharge the greater the ratio indicating a more biologically stable stream. Where stable conditions do apply the ratio is relatively consistent. Many rivers containing considerable amounts of sewage effluent will eventually be used for potable water supplies. It will be of importance to obtain as much information of the soluble organic matter present in the water course. This can be reasonably

accurately computed by using the COD. test as well as the usual BOD. test.

4.2. A CHARGING SCHEME BASED ON THE COD. VALUE.

Since the inception of the Upper Tame Main Drainage Authority in 1965 the charging scheme used has been based on a formula where the organic strength factor was dependent on BOD. and/or PV. The trade effluent consents issued specified allowable limited of these parameters. Trade effluent samples were characterised into classes roughly based on type of industry and only certain classes had a strength factor incorporated in the charging scheme.

For instance, food industries such as bakeries, butcheries, breweries were included in classes with a strength factor. So were factories producing or using organic chemicals such as plastic manufacturers. Industries such as foundries and metal plating were in classes have no strength factor in the charging formula. Of the six classes used, two had strength factors specified. The Authority reviewed the charging system and decided that the classification system should remain. Additionally every class should have a strength factor included in the analysis schedule and that an amended charging formula should apply universally.

Following a considerable amount of exploratory work the decision was taken to use the COD. test and/or the OCV. test as a measure of the organic strength of the effluent. The revised scheme was introduced in 1970.

4.2.1. Where previously only a limited number of the trade effluents required to be analysed for an organic strength value, the problem now faced was of very large numbers of samples required to be

analysed. In addition to the trade effluents it was decided to analyse regular sewage works samples for their COD. value on both the shaken and settled sample. These plus occasional large numbers of sample from the Authority's research projects created a very heavy work load. The total numbers of samples from all sources analysed for a typical 3 months period, 1st April 1972 to 30th June 1972 was 6,100. Together with repeat and duplicate analysis, on samples with COD. values in excess of 1000 milligrams per litre, and including the daily blanks and standards on both manual and the automated procedures a total of 9966 actual analyses were carried out in these 3 months. In a total of 60 working days this meant a daily average of 166 COD. determinations. Unfortunately for laboratory organisation there is no such thing as an average inflow of samples. As oxygen demand tests require rapid analysis it is unwise to store samples to even out the variable daily intake of samples. The maximum and minimum number of determinations carried out on any one day during the 3 months specified were 345 and 68 respectively.

High work loads lend themselves to the use of semi or completely automated analytical systems when available. Procedures, techniques and apparatus have evolved which allows the appropriate laboratory to handle this heavy work load.

4.2.2. The revised charging scheme has been of significance for several reasons. The cost of processing the organic loading has become more evenly spread among traders instead of being excessively loaded against certain classes of trade effluent. This is clear from the COD. demand results on the samples tested since the inception of the revised scheme. They show that a

considerable amount of oxygen demand material is being discharged by traders not subject previously to an organic strength charge.

Another significant point is the wide acceptance of the test as the method of measuring organic loading. The feeling seems to be that the COD. and/or OCV. tests apply fairly and consistently to every trader. They can be accurately checked by the trader if he wishes and obviates the mistrust created by the erratic response of the BOD. and PV. tests when applied to trade effluents.

CHAPTER 5.

DEVELOPMENT OF AN AUTOMATED SYSTEM.

5.1. THE REQUIREMENT FOR AN AUTOMATED SYSTEM.

The need for an automated COD. system was twofold. The initial requirement was for a laboratory instrument to assist with the analysis of large numbers of individual samples. A second requirement was a system for on-stream monitoring of sewage works final effluent discharge. This later requirement is for a system capable of running unattended for long period whereas the laboratory instrument would normally be used only during working hours. The monitoring system was required to supplement an experimental analytical system measuring a range of parameters on the final effluent being discharged from the large sewage disposal works at Minworth, Warwickshire. All the monitoring instruments being housed in a brick hut alongside the channel carrying final effluent being discharged into the River Tame.

For the automated procedure to be acceptable the COD. results must be similar to the result given by the specified manual procedure. This is especially so because of its use for charging purposes for trade effluent samples arising from widely differing sources.

The only way to see if suitable agreement is possible would be by carrying out extensive comparison tests. Should good agreement be unobtainable for trade effluents only the monitoring system would require to be tested. The decision was taken to try and develope an automated monitoring system and to use the system devised to decide if reasonable agreement with manual COD. value

results could be given for both trade effluent and other types of wastewater samples. If so, the basic monitoring system would be modified for laboratory use.

5.2. A CONTINUOUS FLOW AUTOMATED COD. SYSTEM.

When the initial interest in an automated COD. system was shown only the system by Molof and Zalecks (73) and subsequent modifications (74, 75, 76). had been described in the literature.

This system and its modifications employ a basic three part layout. A peristaltic pump is the heart of the system and is used to meter the sample and all reagents into the system using pump tubing of set dimensions. The volumes pumped are not expected to be exact because of pump tube tolerances but must be reproducible over extended periods as must the ratio of the volumes pumped. The pumped solutions are mixed and the mixed solution is fed into the second part of the system. This consisted formerly of a heated rotating glass helix but is now a long glass coil immersed in an enclosed oil heating bath maintained at some appropriate temperature. The heating period is a function of the volume of mixed solution being pumped and the volume of the coil or the digester helix. The mixed solution after heating then passes through colorimeter which measures the change in the percentage transmission of the solution. This change is recorded on a strip chart recorder as a shift in the baseline given by pumping distilled water and sample alternately. The strip chart will show a series of peaks, each representing a sample. By pumping standards of known COD. values the COD. values of the samples can be computed by comparison of peak heights. The colorimeter may be used at either wavelength of 440 nanometres,

which measures the decrease in $Cr_2O_7^{2-}$ ion concentration, or of 620 nanometres, which measures the increase of Cr^{3+} ion concentration. Good correlation was reported between the standard manual procedure and the automated Technicon procedure. Both for individual chemicals and samples from various stages of an industrial waste water treatment plant.

5.3. EXPERIENCE USING A CONTINUOUS FLOW SYSTEM.

Experiments were started using a system based on the Technicon system as described by Adelman (76). to analyse both sewage works samples and trade effluents, received as discrete samples in the laboratory. Additionally it was also hoped to investigate its potential for use as a monitor. The only deviation from the Adelman system was the use of a 15mm. flow cell in place of the 50mm. flow cell specified by Adelman. An alteration in the dichromate strength to offset the change in cell path length was the only deviation from the solutions specified.

Because of the strong sulphuric acid solutions used it is necessary to use 'acidflex' pump tubing which is acid resistant, fluorinated rubber, tubing. The interconnecting tubing in the system must also be acid resistant and is a mixture of glass, P.T.F.E., and acidflex.

5.3.1. The first thing of note was the amount of pressure built up in the system. The very high viscosity of the strong sulphuric acid solution plus the long length of glass coil makes it impossible to pump without a great deal of pressure. The tremendous back pressure built up makes it necessary to ensure very safe connections, as blown joints could, and did on several occasions, spray strong hot acid.

The second point of note was the loss of elasticity of the acidflex pump tubing after relatively short usage. Samples from different deliveries also lost elasticity to show that the fault was inherent in the tubing. The loss of elasticity was shown normally by a gradual fall off in the volume of solution pumped, but on several occasions the tubing abruptly stopped pumping. Though the delivery rate fell, the acidflex tubing was unaffected chemically. The time of failure varied but fall off commenced within 24 hours and the stronger the acid the more rapid the deterioration. This drop in delivery rate has distinct disadvantages. The continuous flow system depends on reproducible pumping of all solutions being maintained all the time and any variation of pumping rate is therefore a serious disadvantage. Besides the acidflex pump tubes, ordinary plasticised P.V.C. tubes are used for pumping the sample and mercury (II) sulphate. As these did maintain their pumping rate the nett affect is a steadily reducing acid concentration in the mixed solution being pumped through the heating coil. The position is eventually reached when the solution starts to boil because the acid strength has dropped too low. The enormous pressure increase could prove dangerous to both operator and the apparatus. On one such occasion, a tubing connection inside the oil bath blew apart causing a leakage of strong acid into the oil bath. The acid lay on the bottom of the oil bath dissolving away the bath lining and had to be neutralised in situ. It was realised the relatively high quantities of reagents required by the system running on a continuous basis would cause difficulties. It would, amongst other things, use about 3 litres of concentrated sulphuric acid every 24 hours. Whitehead and Cooke (82). have indicated the problem with respect to reagents inherent in

continuous autoanalyser monitoring especially at sites remote from the laboratory. A Watson Marlow peristaltic pump was substituted in the system for the Technicon pumps to see if extended pump tube life could be achieved. A definite improvement was noticeable but insufficient to encourage to use of the system for continuous monitoring purposes.

5.3.2. Because the system is based on continuous flow using pump tubing, two further disadvantages inherent in the system were noted. The first one concerned the presence in the sample of detergents, oils and grease. These compounds could have significant COD. values yet probably would suffer some unintentional removal from the sample by adsorbtion on the walls of the pump tubing and the delivery tubing. Not only could this substantially lower the COD. of the sample but leaching off by subsequent samples could enhance the true value of those samples. Analysis of a number of different anionic detergent samples gave automated COD. values up to 30% lower than the manual method results. The shape of the recorder peak showed excessive tailing indicating subsequent leaching of adsorbed detergent.

The other disadvantage was caused by suspended solid matter in the sample. Not only is it difficult to obtain a representative aliquot from a sample cup using a peristaltic pump but also filtration of the solids often occurs inadvertently. As suspended solids contribute substantially to the COD. content of many samples, particularly sewage works samples, low results or cross contamination can occur quite easily.

5.4. AN ALTERNATIVE TO A CONTINUOUS FLOW SYSTEM.

The major drawbacks of excessive reagent usage, solids removal from samples and removal of easily absorbed components from the samples are inherent in the continuous flow system just described. An alternative to this system is to measure out the various reagents as discrete individual aliquots which are mixed, and the mixture then reacted and measured. Such a system would imply the use of a number of automated pipettes or syringes to meter a definite, reproducible reagent or sample volume on command. The command and order of reagent addition would be time based using a timer control such as a cam timer. The system envisaged was a part discrete, part continuous combination. Automated syringes would be used to meter samples and reagents into a mixing vessel. The mixed solution would then be pumped by a single pump tube through the heating bath, and then through the colorimeter in the same manner as that used in the Technicon system. The system was initially tested by manually pipetting and mixing either sample, standard or distilled water blank with the required volume of digestion solution. No mercury (II) sulphate solution was added in these initial experiments. The volume ratio used was 2.5 ml. of sample, standard or distilled water mixed with 7.5 ml. of 90% Sulphuric Acid. This contained dissolved potassium dichromate as the oxidising agent and silver sulphate as the reaction catalyst. The retention time depended purely on the pumping rate and the volume of the heating coil and was independent of the period of pumping. Approximately 3 minutes pumping of each sample or standard mixed solution was given followed by 3 minutes pumping of the 'blank' mixture, using a pumping rate of approximately

2.0 ml. per minute. The solutions being pumped were air segmented, using a pump tube to introduce air bubbles into the mixed solution, before they entered the heating coil. From a calibration graph of peak height against the COD. value for the standard, the COD. value of the unknown samples were computed and compared with the results for the same samples using the manual procedure. A temperature of 155°C. was used for the heating bath and the retention period of the solution in the heating bath was approximately 20 minutes. Table 5. shows some typical results given for shaken final effluents. Average results are given for the manual analysis which were carried out in duplicate. The average of a number of replicate results are given for each sample using the partialy automated procedure.

TABLE 5.

COMPARISON OF COD. VALUES BY THE MANUAL PROCEDURE WITH RESULTS USING A PART AUTOMATED PROCEDURE AFTER MANUAL MIXING.

SHAKEN FINAL EFFLUENT SAMPLES TAKEN FROM THE SAME SEWAGE WORKS.	AVERAGE COD. RESULT (mg/litre)	
	MANUAL PROCEDURE	PART-AUTOMATED PROCEDURE
1	120	139
2	70	98
3	90	128
4	85	108
5	75	160
6	60	89
7	65	98

The agreement was not very good but sufficient to encourage further work. What was noticeable was that replicates by the part automated procedure showed much better agreement between

themselves than the semi-micro manual results.

In order to eliminate the possibility of error due to the presence of chloride, the premixed solution used in the part automated procedure was modified by the addition of 0.25ml. of 10% mercuric (II) sulphate to the sample before addition of the digestion solution. Table 6. shows the results given by the two procedures for final effluents from a number of different sources.

TABLE 6.

FURTHER COMPARATIVE RESULTS BETWEEN THE MANUAL AND THE PART AUTOMATED COD. PROCEDURES.

FINAL EFFLUENT SAMPLE	AVERAGE COD. RESULTS IN MILLIGRAMS PER LITRE	
	MANUAL PROCEDURE	PART-AUTOMATED PROCEDURE
Minworth 1	120	98
" 2	70	100
" 3	90	105
" 4	85	80
" 5	75	89
" 6	60	74
Coleshill 1	52	97
" 2	97	115
Oldbury 1	44	75
" 2	46	57
" 3	44	82

The mainly higher results produced by the part automated system were difficult to explain as this would mean greater oxidation using a system with a much shorter heating period.

An investigation into the manual procedure showed that a serious error had been introduced into the laboratory method sheet.

Instead of prescribing the use of 5.0 ml. of sample or prediluted sample the procedure stated that 5.0 or 10.0 ml. of sample could be used. If 10.0 ml. of sample was used the acid concentration in the final mixture would be reduced, giving a drastic reduction in the reflux temperature and a probable reduction in the extent of oxidation.

This reduction in oxidation would be particularly noticeable with final effluents and other samples which had received some degree of oxidation treatment. Most of the more easily oxidised compounds would already have been removed.

The knowledge that final effluents would have a high proportion of difficult to oxidise compounds led to using the part automated system in a comparative exercise with different retention times being used in the heating coil. The retention time in the coil being doubled to approximately 40 minutes by reducing the pumping speed of the multispeed Watson-Marlow peristaltic pump used to pump the mixed solutions. The COD. manual method was used to check analyse the samples.

The most interesting point is the enhanced results given by the extra 20 minutes heating which either indicated increased oxidation, or greater decomposition of dichromate. These and other similar results were sufficiently encouraging to proceed with building a completely automated system based on the part automated system. This system, if successful, would overcome the problems of homogeneous sampling of solids, excessive usage of reagents, and pump tube failure found with the completely pumped system. Low results, caused by adsorbtion of detergents, greases and oils on sample pump tubing would also be largely overcome by discrete sampling.

TABLE 7

COD. VALUES FOUND USING DIFFERENT HEATING PERIODS IN THE AUTOMATED PROCEDURE.

FINAL EFFLUENT SAMPLE	COD. IN MILLIGRAMS PER LITRE		
	MANUAL PROCEDURE	PART-AUTOMATED PROCEDURE	
		40 MINUTE HEATING	20 MINUTE HEATING
Minworth 1	70	75	65
" 2	90	156	86
" 3	85	73	66
" 4	75	109	56
" 5	60	57	60
" 6	65	57	62
Coleshill 1	52	80	59
" 2	101	82	77
Oldbury 1	45	73	56
" 2	47	68	54
" 3	44	65	52

5.5. A PART DISCRETE, PART CONTINUOUS FLOW AUTOMATED SYSTEM.

The system visualised consisted of a part discrete and a part continuous flow system. Automated syringes would be used to measure and dispense the reagents and samples into a mixing pot. From this the mixed solution would be pumped, on an alternate basis with a blank/ baseline reagent, into the remainder of the system. Figure A. shows the schematic layout of the proposed system. Using a cam timer as the controller, a set cycle of operations could be programmed to repeat over any fixed time cycle required to very close tolerances. Where possible the system used commercially available equipment which was modified if necessary.

5.5.1. Items used in the automatic system:

A) Sample dispenser diluter wired for remote control, supplied by Hook and Tucker, England.

B) Super-spenser, for dispensing the digestant, wired for remote control. Super-spenser is a registered trade name for a dispenser made by Hook and Tucker, England.

C) and (D). Motorized valves wired for remote control, supplied by Hook and Tucker, England.

E) Fluidized sand bath, supplied by Techne, England.

F) MHRK/72 flow inducer, supplied by Watson Marlow, England.

G) Vitatron UC 200 colorimeter, supplied by Fisons, England.

H) Vitatron UR 300 LOG/LIN recorder, supplied by Fisons, England.

I) 15 ml. glass mixing pot.

J) Super MSC. cam timer, supplied by Electrical Remote Control, England.

K) Pivoting sampling arm.

5.5.2. The system is programmed so that the entire analytical sequence is completed once during one cycle of the cam timer. Each operation is controlled by one of the cam timers independently variable cams. The sequence is as follows:-

1) The sampling arm dips the sampling probe into the sample.
2) The dispenser diluter A. operates taking up sample via the sample probe. 5 seconds later the sample arm lifts the sample probe out of the sample cup. The sample arm swings over and drops the sample probe into the mixing pot.
3) The dispenser diluter is activated and ejects the sample into the mixing pot followed by mercury (II) sulphate solution acting as a wash/diluter down the same tube. This ensures complete transfer of sample and minimizes cross contamination of samples.
4) The sample arm returns to its position above the sample and remains there until the sequence restarts.
5) After step (3) dispenser B. Fig. A, adds digestion solution to the mixing pot. Complete mixing is produced by agitation with a stream of purified air.
6) The motorized valve D., which had been allowing the pump to take the premixed blank/baseline solution, switches over cutting off the blank/baseline solution. This allows instead the mixed solution to be pumped from the mixing pot into the heating coil. Both solutions, which are air segmented, are pumped at a rate of about 1.0 ml/min.
7) Valve D. reswitches to its original position cutting off the flow of mixed solution to the pump and allows the blank/baseline solution to again be pumped into the heating coil.
8) Shortly after the start of step (7) valve C. operates. This allows the excess mixed solution in the mixing pot to be

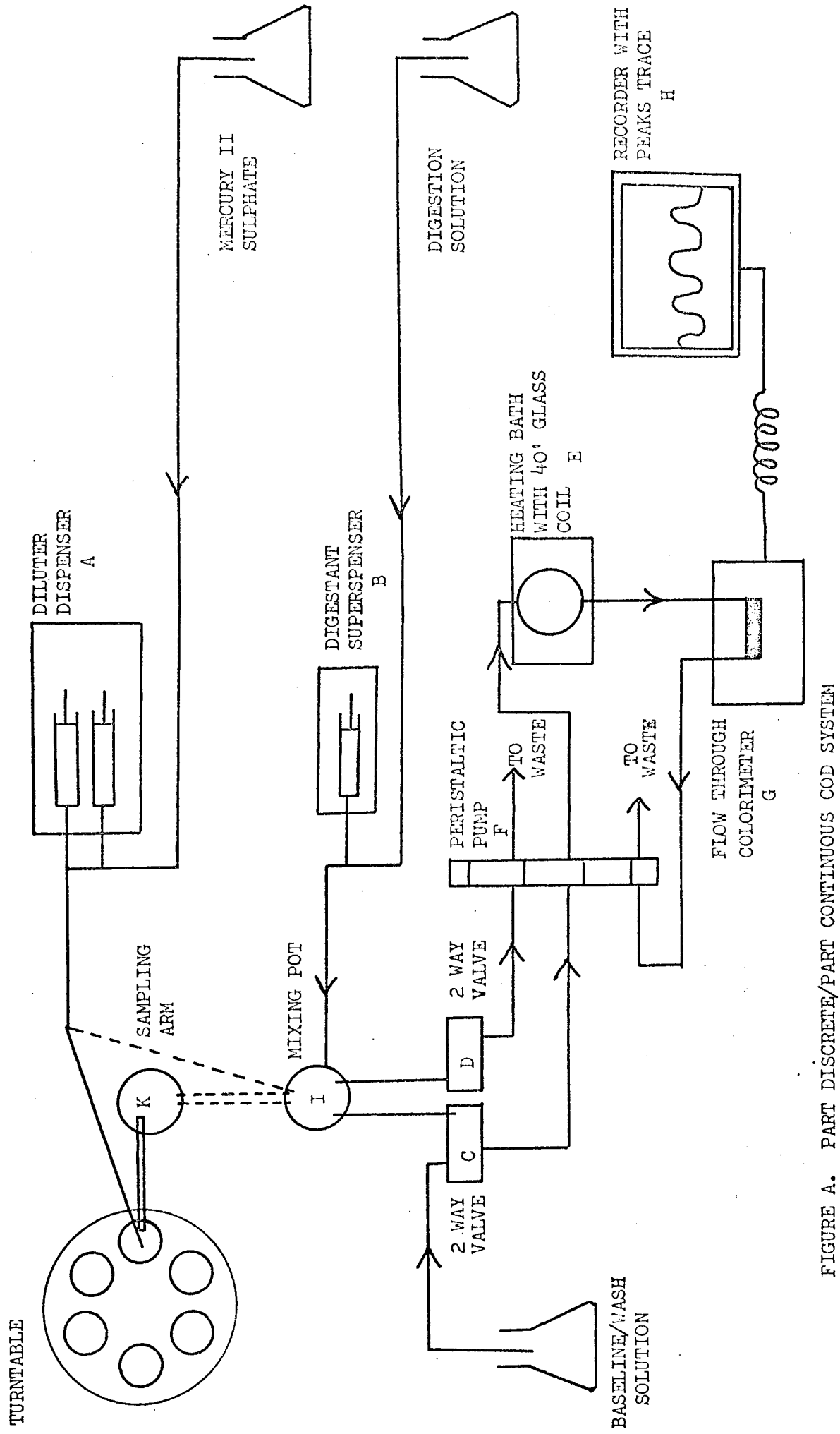


FIGURE A. PART DISCRETE/PART CONTINUOUS COD SYSTEM

to be completely pumped to waste.

9) Valve C. re-switches leaving the mixing pot empty.

10) The cam timer completes its cycle and commences another cycle at step (1).

The peristaltic pump drives the air segmented solutions through the heating coil to a small separator made on a cascade system. The air bubbles are released as the solution leaving the heating coil falls into a small cascade and collects in a small depression. The major part of the collected solution is drawn through a 10 mm. Hellma flow-through cell, fitted in the colorimeter, by the peristaltic pump. Excess sample cascades over the lip of the depression to waste.

5.6. ASSEMBLING THE SYSTEM.

The items comprising the system shown in Figure A. were assembled. Some of the items were already available in the laboratory, some required to be purchased and modified and some required to be designed and built.

The basic flow-through part comprising the peristaltic pump through to the recorder was already assembled. The automatic dispensers, the turntable, and the cam timer required to be purchased and the sampling arm designed and constructed The function and the facilities of the various items are further explained.

5.6.1. The colorimeter and recorder are matched items designed to be used in conjunction with one another as well as being separate instruments usable by themselves. The colorimeter is a single beam instrument with two different photocells to

give a more effective cover over its wide wavelength range. The light source is chopped to produce an alternating output signal from the photocell. The cell holder is designed to accommodate 'Helma' type flowthrough cells of either 10 or 20 millimetre lightpath length and narrow band filters are used to select the wavelength required. In this system the colour density due to the $Cr_2O_7^{2-}$ ion is measured at a wavelength of 440 nanometres. The signal from the photocell is amplified by the colorimeter and fed to the recorder. The recorder can either record the signal direct as percentage transmission values, or by internal circuitry linearise the logarithmic percentage transmission values into optical density values. Using this latter facility the peak heights given on the strip chart were linear with respect to the COD. value of the sample. A plot of peak height against COD. for standards gives a linear calibration graph. This facility is of great value for the system where the value being measured is the reduction in colour density due to the $Cr_2O_7^{2-}$ ion. The recorder has the facility of offsetting the colorimeter signal received. So tracing the peak for the signal value received on whichever part of a strip chart the operator wishes. Additionally, the peak heights recorded can be amplified, by any value up to a maximum of about a factor of four, enabling the COD. range measurable on the strip chart to be easily altered.

5.6.2. A fluidized sand bath is preferred to the conventional oil bath for heating purposes. It does not present a fire hazard, and can be rapidly heated or cooled. The selected bath temperature can be closely controlled using the separate temperature controller available with the bath. The sand bath is also unaffected by hot acid spillage caused by breakage of the coil or its joints,

because the sand is capable of absorbing large quantities of spillage without any ill effects. The air for fluidisation of the bath can be either by laboratory compressed air supply or by use of an associated pump designed for the purpose available from the manufacturers.

5.6.3. The peristaltic pump incorporates a delta shaped rotating arm which is sheathed in PTFE. to reduce wear on the pump tubes. The pumping life of the tubes is normally found to be in the order of 60 hours of actual use. However, as a safety margin they are changed after 48 hours use. Pump tubes were often found to stop pumping abruptly and not fail gradually.

Variations in pumping rate within quite large limits is of no consequence provided more sample is being pumped through the heating coil than is being taken off through the flow cell. Otherwise air is drawn into the flow cell.

5.6.4. The Hook and Tucker super spenser appeared at the time the only available automatic dispensers capable of handling the extremely corrosive, highly viscous, sulphuric acid/dichromate mixture. Though the dispenser was normally operated by manual activation of a push button or foot switch, it was easily modified to enable remote operation from a microswitch on the cam timer. The changeover valves from these dispensers were available separately as motorised items and were employed as the two way valves in the system, again after modification to allow for remote operation.

5.6.5. The diluter dispenser supplied by the same firm was again easily modified to allow operation by remote control. It differed in this respect from the other two items in requiring

two separate signals, one for the intake stroke and a second for the ejection stroke.

The diluter dispenser has an adjustable volume syringe. This on withdrawing sucks the set volume of sample into a small glass coil, situated between the sample probe and the dispenser, and holds it there. No sample enters the syringe. The action of withdrawing this syringe is followed immediately by the withdrawing action of a second adjustable syringe which takes up the mercury (II) sulphate diluent via a separate piece of tubing. The two syringes are on the same cam but are offset from each other to produce the time delay. On the dispensing cycle the first syringe operates, delivering the sample from out of the small glass coil into the mixing pot. The second syringe then operates and by means of a changeover valve ejects its volume of diluent down the same sample tube into the mixing pot, so ensuring good sample transfer.

5.6.6. The super M.S.C. cam timer was chosen as a suitable timer/process controller. It possesses thirteen independently adjustable cams and a time cycle which can be varied by the use of different gearing ratios, and/or drive motors of different speeds.

5.6.7. The sampling arm was designed and constructed so as to lower the pick up probe into the sample and lift it clear when required on a command signal from the cam timer. The arm was pivoted on a reversible direction motor to allow it to swing between the sample and the glass mixing pot. The design and construction of the arm has been described by Phillips (83).

5.6.8. A turntable was also required for laboratory tests to hold the sample cups. A fraction collector type 105A, manufactured by the London Ignition Company, England was used for the purpose. This turntable had wired-in contacts which, when activated from a remote source, allowed the table to move on one position. The turntable could be supplied drilled with holes for sample cups as specified by the purchaser.

5.6.8. The system was assembled as described when all the items had been received, and modified where required, and the system put under test.

5.7. USE OF THE PART DISCRETE, PART CONTINUOUS SYSTEM.

Numerous small faults arose during the first trials of the system both on the instrument and the chemical technology side. Most proved relatively easy to overcome but were time consuming to rectify. Some typical faults were:

A) The incorrect microswitches supplied with the cam timer caused the drive unit to stall.

B) Incorrect material in O rings in the dispensers caused them to be attacked by the acid mixture and breakup causing the leakage of acid into the dispensers.

C) The relay on the temperature control system on the fluidised sand bath went inoperative when contacts welded together through overheating.

D) Insufficient cooling of the heated acid solution from the heating bath caused the flow cell to crack.

E) One of the most frequently recurring faults was the blowing of joints on interconnecting tubing. Glass, PTFE, and fluorinated tubing were all employed for this purpose and

joints capable of withstanding very high pressure were difficult to form between these different materials.

The chemical technology also posed some initial problems. The mercury (II) sulphate was added to the sample as the diluent in the diluter dispenser which saved using a separate super spenser for this purpose. Excessive additions to the reagent caused depositions of the incompletely soluble mercury (II) sulphate in the heating coil and eventual complete blockage. Blockage also occured in the tubing after the heating bath and in the flow cell.

5.7.1. On the chemical technology side the most important question was to decide on the period for a complete cycle. The system was designed initially to be used for on-stream monitoring of final effluent from a sewage works. It was, if possible, to be used first on the final effluent of the Minworth Works of the Upper Tame Main Drainage Authority. Because of the very large discharge from the works, the quality of the effluent is not subject to violent fluctuations in quality, but rather shows gradual deviation. Therefore, although continuous monitoring is desirable, it is not a genuine necessity. The initial time cycle was chosen as fifteen minutes, this meant a sample was taken and analysed four times per hour and 96 times in 24 hours, and should be more than sufficient to give the correct indication of changes in effluent quality. No matter what the time cycle is, the reaction time in the heating coils would remain dependent upon the coil length, and the rate of pumping of the mixed solution through the heated coil. With probable fall-off of pumping rate the consequent variation in heating period would pose one of the most serious problems to the system.

5.7.2. Poor mixing between the aqueous solutions and the very viscous acid solution was overcome by blowing a continuous stream of air bubbles through the mixing pot to give complete mixing. It was not realised for some time that the unpurified air was responsible for introducing the puzzling high random errors frequently found in the first trials. Subsequently the air was purified by bubbling through a sulphuric acid/dichromate wash solution.

5.7.3. Fall off in the volume of the solution being pumped created another problem when the relatively increased air percentage being pumped expanded in the heating coil causing still higher pressures to be exerted on the joints.

5.7.4. The sample probe dipping into the sample contained mercury (II) sulphate wash solution in 10% v/v sulphuric acid. Because of the higher density of this solution over purely aqueous samples it was found that diffusion between the solutions was occuring, to a variable extent, and was causing non reproducible aliquoting and sample overlap problems. A tee joint was made about 1 inch from the tip of the sampling probe through which air was blown for a few seconds, after the transfer of sample and diluent to the mixing pot. This created an air gap in the end of the probe dipping into the sample which effectively prevented diffusion.

5.8. CHOICE OF A SUITABLE DIGESTION SOLUTION.

Initial experiments with the completed system were designed to find suitable working parameters. Potassium hydrogen phthalate was chosen as a suitable standard. It is available as a pure solid, easily soluble, forms a stable solution and is easily

oxidised under the conditions of the various COD. tests. It was necessary to investigate the various reagent ratios and solution strengths to find the most suitable for the system. The manually mixed ratio of 2.5 ml. of sample mixed with 7.5 ml. of sulphuric acid, containing potassium dichromate and silver sulphate, was used as a guide. However, to offset the effect of chloride present in the sample, the diluter dispenser was set to dispense 2.0 ml. of sample plus 0.5 ml. of 1% w/v mercury (II) sulphate in 10% v/v sulphuric acid solution. The acid strength of digestant previously used was 90% v/v sulphuric acid. It was decided to test the procedure using digestant containing varying amounts of both sulphuric acid and potassium dichromate. A stock digestion solution containing 7.5g. of silver sulphate and 3.2 g. potassium dichromate per litre of concentrated sulphuric acid was prepared. Three different mixtures of this stock digestion solution with sulphuric acid and water were prepared and 7.5 ml. volumes of each of the three mixtures was tried as the digestion solution. The mixtures were as follows.

Digestion solution (I): 125 ml. of stock digestion plus 800 ml. of concentrated sulphuric acid plus 75 ml. of distilled water. This solution is 92.5% v/v sulphuric acid and when 7.5 ml. is mixed with 2.5 ml. of sample/diluent the acid strength is 73% v/v sulphuric acid. The potassium dichromate strengths are 0.4 and 0.3 g. per litre respectively.

Digestion solution (II): 125 ml. stock digestion solution plus 725 ml. of concentrated sulphuric acid plus 150 ml. of distilled water. This solution has a sulphuric acid strength of 85% v/v before sample/diluent addition and 63% v/v after

addition. The potassium dichromate strengths are similar to those of digestion solution (I).

Digestion solution (III): 250 ml. of stock digestion solution plus 600 ml. of concentrated sulphuric acid plus 150 ml. of distilled water. This solution has the same acid strengths as digestion solution (II) but double the potassium dichromate strength, namely 0.8 and 0.6 g. per litre respectively.

The blank/baseline solutions were made up by premixing each digestion solution with distilled water in the ratio 3:1.

A set of final effluent samples from the same sewage works, taken at hourly intervals were analysed by the new system using all three digestion solutions and by the standard manual procedure. The COD. results quoted as milligrams per litre are shown in Table 8.

The figures show that digestion solution (II) gave the closest agreement with the manual procedure results. This digestion solution is the weakest of the three and it is noteworthy that the other two reagents nearly always gave higher results than the manual procedure.

A set of samples from various points taken during a river survey were analysed using the new automated procedure with digestion solutions (I) and (II) and also for further comparison with the Technicon procedure. Many of the samples contained considerable amounts of suspended solids. Though the samples were kept in suspension when the aliquots were taken it was noticeable that some solids were being inadvertently filtered out using the Technicon system. This was the main cause of

TABLE 8.

COMPARISON OF DIFFERENT DIGESTION SOLUTIONS

FOR DETERMINING COD. VALUES.

HOURLY SAMPLES	AUTOMATED METHOD			MANUAL METHOD
	DIGESTANT(I)	DIGESTANT(II)	DIGESTANT(III)	
9 a.m.	100	102	110	111
10 a.m.	110	96	100	84
11 a.m.	99	92	91	82
12 noon	85	87	85	90
1 p.m.	85	87	85	90
2 p.m.	92	88	98	83
3 p.m.	87	82	93	83
4 p.m.	101	84	105	84
5 p.m.	85	82	119	88
6 p.m.	92	85	110	95
7 p.m.	102	82	106	84
8 p.m.	100	79	108	86
9 p.m.	100	81	111	83
10 p.m.	166	83	91	80
11 p.m.	107	84	96	82
12 p.m.	99	87	94	82

their much lower results, when using this system, shown in table 9. The results, quoted in milligrams per litre COD., also show reasonable agreement despite high solids between the results of the two digestion solutions being tested. Again the results using digestion solution (III) were higher than those using digestion solution (II).

TABLE 9.

COMPARISON BETWEEN THE TECHNICON AUTOMATED SYSTEM AND THE EXPERIMENTAL AUTOMATED METHOD

SAMPLE		TECHNICON METHOD	AUTOMATED METHOD	
			DIGESTANT(II)	DIGESTANT(III)
River Tame at Saltley	1	99	111	126
	2	85	111	130
	14	52	127	128
	17	55	120	130
	20	72	122	135
	22	55	130	134
	23	50	121	125
Minworth Final Effluent	1	70	153	169
	4	61	150 167	162
	7	46	104	118
	11	49	143	153
	20	70	118	122
	24	75	152	168
River Tame Bromford Bridge	1	56	128	140
	4	44	92	105
	6	51	128	144
	13	49	129	123 134
	16	49	107	112 112
	18	81	184	201 206
	22	96	184	235 208
River Tame Lea Marston	1	64	123	116 123
	4	107	200	259 276 272
	7	57	128	131 145

Using 2.0 ml. of sample and 0.5 ml. of mercury (II) sulphate with 7.5 ml. of digestion solution (I) or (II) gave a range of 0-200 milligrams per litre COD. Samples above 200 milligrams per litre completely exhausted all the dichromate present. It was therefore decided to increase the concentration of stock digestion solution in the working digestion solution from 12.5% to 15%. This gave a reasonable excess of dichromate, with a concentration of 200 milligrams per litre COD. in the sample. The effect of this slight increase in concentration of potassium dichromate was investigated, A further series of Minworth final effluent samples were analysed using this new digestion solution (IV) and compared with the manual method. Table 10 gives the results found in milligrams per litre. The correlation between the results was very good. It was provisionally decided to use this digestion solution (IV) for the on-stream automated system. This digestion solution would adequately cover the range 0-200 milligrams per litre COD. It contained also sufficient sulphuric acid to raise the boiling point of the mixture above the range of about 155-165^{o}C proposed for the temperature of the sand bath. Table 11. shows some of the results given by the new system using the digestion reagent (IV). The samples used were effluents from laboratory experimental aeration units and final effluents from a number of different sewage disposal works. The agreement with the standard manual procedure results was again good. It was concluded that the proposed automated analyser, as used for tables 9, 10, 11. and using the digestion solution (IV), is suitable for analysing final effluent and river samples of varying quality.

TABLE 10.

EXPERIMENTAL AUTOMATED SYSTEM USING DIGESTION SOLUTION (IV).

SAMPLE	TIME	AUTOMATED METHOD	MANUAL METHOD
Minworth Effluent	1 a.m.	102,103	90
	2 a.m.	104	94
	3 a.m.	100, 97	96
	4 a.m.	107	100
	5 a.m.	98	100
	6 a.m.	218,221,236	230,245
	7 a.m.	96	97
	8 a.m.	93, 97	109
	9 a.m.	84	86
	10 a.m.	108	109
	11 a.m.	107	113
	12 noon	121,100,104	122
	1 p.m.	96	95
	2 p.m.	97,100	103
	3 p.m.	87, 93	95
	4 p.m.	99, 93	86
	5 p.m.	92, 84	85
	6 p.m.	79, 82	81
	7 p.m.	83, 71	81
	8 p.m.	75	77
	9 p.m.	75	71
	10 p.m.	78	77
	11 p.m.	83, 87	71
	12 midnight	82, 82	101

TABLE 11.

FURTHER RESULTS USING DIGESTION SOLUTION (IV)

COMPARED WITH MANUAL METHOD RESULTS.

SAMPLE		AUTOMATED METHOD	MANUAL METHOD
Research Laboratory Final Effluents.	58/1	211,176	170,195
	58/2	174	158
	58/3	179	156
	58/4	128	125
	58/5	154	130
	58/6	105	101
	59/1	159	147
	59/2	184	159
	59/3	345	370
	59/4	183	179
	59/5	248	249
	59/6	181	191
	60/A	208	211
	60/B	229	217
Coleshill Mixed Final Effluent to River		63	56
Coleshill Final 1 Effluent		177	166
Coleshill Final 2 Effluent		102	80
Coleshill Final Effluent		70	70
Norton Green Final Effluent No. 2. Grass Plot		51	48
Coleshill Mixed Final Effluent Unit 3		52	54
Oldbury 1, 2 and 3 Humus Tank Final Effluent		80	87
Oldbury No. 4 Humus Tank Final Effluent		81	96,92
Oldbury Nos. 5 and 6 Humus Tank Final Effluent		79	86
Woodgate Final Effluent		50	52
Tividale Final Effluent (Old Works)		76	83
Tividale Final Effluent (New Works)		86	81

5.9. AUTOMATED ANALYSIS APPLIED TO TRADE EFFLUENTS.

It was also intended that the system be used, if successful, as a laboratory based instrument for analysing discrete samples from the sewage disposal works and also trade effluent samples. A few selected trade effluent samples known to have very high COD. values were diluted and analysed by the new automated procedure and by the standard manual procedure. Table 12. shows there was good agreement, for the samples tested, between the two procedures. The table quotes the COD. values found in milligrams per litre.

TABLE 12.

COMPARISON OF MANUAL AND AUTOMATED COD. VALUES FOR DISCRETE TRADE EFFLUENT SAMPLES.

SAMPLE	DILUTION	AUTOMATIC METHOD	MANUAL METHOD
T.E.No.14974	X 1/100	22,300	24,000
	X 1/200	21,800	23,300
T.E.No.14975 Solvent Recovery	X 1/25	5,075	5,350
	X 1/50	5,050	5,110
T.E.No.14976	X 1/4	985	1,170
	X 1/10	1,000	—

The method would appear suitable for high COD. value samples if diluted sufficiently. This dilution step is an obvious disadvantage even if a suitable dilution was known which is not likely. However, dilution does reduce high chloride levels if present which would otherwise interfere in the undiluted state.

For the purpose of a laboratory based instrument dealing with a wide range of discrete samples the range 0-200 mg/l is possibly too small. Too wide a range would, however, not give the sort of accuracy desirable especially for samples with low COD. values. As a preliminary compromise a range of 0 to about 600 milligrams per litre was selected. To achieve this, the percentage of stock digestant in the digestion mixture was increased, the amount of sample aliquot was reduced and the volume of mercury (II) sulphate diluent increased. The sulphuric acid strength remained unchanged.

To make the new digestion solution, (V), 250 ml. of stock digestant, 600 ml. of concentrated sulphuric acid plus 150 ml. of distilled water are mixed together. Using 1.0 ml. of sample, 1.5 ml. of mercury (II) sulphate diluent, and 7.5 ml. of digestion solution a straight line graph of peak height against concentration in milligrams per litre COD. was given.

A selection of the worst looking trade effluents received for analysis were analysed after dilution to lie within the range 0-600 milligrams per litre COD. The diluted sample was also analysed by the manual standard procedure as a direct comparison. Considering the poor appearance of many of the samples good agreement was normally found. Table 13. shows the results found in milligrams per litre COD.

Sample 16678 possessed a thick floating layer of oil equivalent to about 20% of the sample. It was impossible to obtain homogeneous samples.

Where poor agreement between the automated and manual methods occurred, a second analysis by both methods was carried

TABLE 13.

COMPARISON OF MANUAL COD. VALUES AND AUTOMATED COD.

VALUES USING DIGESTION SOLUTION (v)

SAMPLE REFERENCE NUMBER	DILUTION	AUTOMATIC SYSTEM	MANUAL SYSTEM
15909	Nil	110	90
14520	Nil	449	428
14544	x 10	2520	2120
14477	x 10	2145	2475
15110	x 2	562	586
14281	x 2	656	616
15980	Nil	44	43
14518	x 4	980	1072
5124	x 10	4000	4080
5134	x 2	740	884
15654	x 2	540	544
15811	x 2	908	856
14397	Nil	134	134
4873	x 10	3300	3400
15745	x 40	10575	11700
5038	x 10	1784	1932
5026	x 100	18200	18800
16021	x 4	764	784
5068	x 4	672,962	662,668
16238		275,564	296,308
16678	x 100	60000	20600
16473	x 2	636	520
16819	x 2	740	784
13972	x 10	1424,1370	1048,1484
16654	Nil	234	256
16640	Nil	192	220
16639	Nil	210	242
17324	x 10	1044	1072

out and both results quoted. Non homogeneous aliquots appear responsible for most erroneous results.

5.9.1. Selected samples from Table 12. having relatively high solids content were filtered through a No. 41 whatman filter paper to remove filterable solids and the filtrates analysed by both the automated and the manual methods. Dilutions, when required, were as quoted in the previous table. Both sets of results showed mainly very good agreement. The high contribution of the solids to the COD. value found for many of the samples can be seen from the figures quoted as milligrams per litre COD. in table 14.

TABLE 14.

THE COMPARISON BETWEEN FILTERED AND UNFILTERED TRADE EFFLUENT SAMPLES

SAMPLE NO.	AUTOMATIC METHOD		MANUAL METHOD	
	FILTERED	UNFILTERED	FILTERED	UNFILTERED
13972	512	1424,1372	520	1484,1048
16422	150	192,198	171	184,193
16424	640	1960	530	1660
16293	136	710	142	732
16546	2220	3160	2240	3230
16377	184	365	190	320
17056	392	482	380	492
16274	181	383	159	448
16331	72	310	39	468
16273	1920	2970	2010	2910
16307	14900	18500	11600	16200

5.10. AUTOMATED ANALYSIS FOR HIGH COD. VALUES.

It was not known what percentage of samples received would have COD. values in excess of 600 milligramms per litre and therefore require pre-dilution. By measuring the colour density due to Cr^{3+} produced from the $Cr_2O_7^{2-}$ during the course of the

COD. test a system capable of measuring considerably greater COD. levels is possible. Using a wavelength of 610 nanometres there is no interference from residual $Cr_2O_7^{2-}$ colour. The extinction coefficient for this Cr^{3+} measurement is considerably lower than for the $Cr_2O_7^{2-}$ measurement at 440 nanometres. Much greater potassium dichromate concentrations can be employed in the digestion solution and consequently much higher COD. values analysed without prior dilution.

The system was not extensively investigated. It was thought the percentage of samples would not justify an additional system nor the trouble of modifying the low range system to utilize it for both high and low range analysis.

Some samples were analysed by a high level procedure. The digestion solution used consisted of 850 ml. of the stock digestion solution mixed with the 150 ml. of distilled water. The volumes used were similar to the volumes for the 0-600 milligrams per litre range. These were 1 ml. of sample, 1.5 ml. of diluent and 7.5 ml of digestion solution. Table 15. shows the comparison found for these samples by both high and low level procedures. For the high level procedure only samples with a COD. of more than 2,500 milligrams per litre were pre-diluted. All results are quoted in milligrams per litre COD.

The agreement was sufficiently close with most samples to indicate that a high level system could at some future date be introduced if necessary. It was only samples of poor physical appearance which gave poor agreement.

TABLE 15.

COMPARISON OF HIGH AND LOW LEVEL AUTOMATED COD. PROCEDURE

SAMPLE REFERENCE NUMBER	COD. FOUND BY THE HIGH LEVEL SYSTEM	SAMPLE DILUTION FOR LOW LEVEL SYSTEM	COD. FOUND BY THE LOW LEVEL SYSTEM
15909	Nil	Nil	110
14520	510	Nil	449
14544	2920	x 10	2520
14477	2050	x 10	2145
15110	730	x 2	562
14281	750	x 2	656
15980	Nil	Nil	44
14518	1450	x 4	980
5124	3910	x 10	4000
5134	960	x 2	740
15654	660	x 2	540
15811	1060	x 2	908
14397	190	Nil	134
4873	3440	x 10	3300
15745	11640	x 40	10575
5038	1960	x 10	1784
5026	18800	x 100	18200
16021	1180	x 4	764
5068	860	x 4	672,962
16238	480		275,564
16473	800	x 2	636
16819	890	x 2	740
13972	1320	x 10	1424,1370
16654	200	Nil	234
16640	200	Nil	192
16639	390	Nil	210
17324	1120	x 10	1044

5.11. SUPPRESSION OF CHLORIDE INTERFERENCE WITH MERCURY(II) SULPHATE.

The high level system was used to test the effect of chloride on the COD. system and to determine what levels of chloride could be tolerated without resorting to dilution or chloride removal.

Instead of the ratio of 1.0 ml. of sample to 1.5 ml. of 1% mercury (II) sulphate diluent previously used in the high level system, manually mixed solutions of different ratios were tested. Initially 0.5 ml. of sample was mixed with 2.0 ml. of 1% mercuric (II) sulphate but this amount of the mercuric (II) sulphate proved insoluble in the final mixed solution. Instead of 0.5 ml. aliquots of sample plus 2.0 ml. of 0.5% mercuric (II) sulphate was used. It was claimed by Dobbs and Williams (53). that each mg. of chloride requires 10 mg. of mercury (II) for complete elimination of the chloride.

∴ 2.0 ml. of 0.5% mercuric (II) sulphate will effectively supress 1,300 milligrams per litre in the sample.

Table 15 shows the results for a number of potassium hydrogen phthalate solutions having a COD. value of 1,000 milligrams per litre containing varying levels of chloride. It is interesting to note that there is a suppression of chloride interference in excess of the calculated figure. It appears there is suppression but not elimination of chloride interference which was also the conclusion of both Cripps and Jenkins. (71). and Burns and Marshall (83).

TABLE 16.

THE SUPPRESSION OF CHLORIDE INTERFERENCE.

POTASSIUM HYDROGEN PHTHALATE SAMPLE	MILLIGRAMS PER LITRE OF CHLORIDE IN SAMPLE	MILLIGRAMS PER LITRE COD. FOUND		
1000 milligrams per litre. COD. value.	250 $^-$	990	1060	1180
	500 $^-$	1050	1100	1200
	750 $^-$	-	1090	1220
	1000 $^-$	1170	1180	1220
	1250 $^-$	-	1210	1240
	1500 $^-$	1230	1220	1270
	2000 $^-$	1250	1280	1300
	2500 $^-$	1300	-	-

To determine the correct Hg^{++}: Cl^- ratio for elimination of chloride interference standard solutions of potassium hydrogen phthalate containing known amounts of added chloride were analysed by the above method. Varying amounts of mercury (II) sulphate were added then water to a total volume of 2.5 ml.

*The sample containing no added $HgSO_4$ gave a precipitate AgCl on adding the digestant. Part of this precipitate was still in suspension when the reaction mixture passed through the flow cell of the colorimeter with the result that the peak produced was very irregular. The COD. value quoted for this sample is the probable value; added height of the peak due to solids was ignored.

** With this sample mercury (II) sulphate was precipitated on adding the digestion solution.

TABLE 17.

THE SUPPRESSION OF CHLORIDE INTERFERENCE USING DIFFERENT Cl^- : Hg^{++} RATIOS

COD. IN MILLIGRAMS PER LITRE OF POT. HYD. PHTHALATE	MILLIGRAMMS OF CHLORIDE IN SAMPLE ALIQUOT	VOLUME ML. OF 1% MERCURY (II) SULPHATE	MILLIGRAMMS OF MERCURY (Hg^{++}) ADDED	RATIO OF Cl^- : Hg^{++} IN MIXTURE	COD. IN MILLIGRAMMS PER LITRE FOUND EXPERIMENTALLY
1000	1.0	0	0	1 : 0	1,380*
1000	1.0	0.5	3.4	1 : 3.4	1,120
1000	1.0	1.0	6.8	1 : 6.8	1,060
1000	1.0	1.5	10.2	1 : 10.2	1,070**
2000	0.5	0.25	1.7	1 : 3.4	2,150
2000	0.5	0.5	3.4	1 : 6.8	2,080
2000	0.5	1.0	6.8	1 : 10.2	2,050
2000	0.5	1.5	10.2	1 : 20.4	2,020

The results in Table 17. shows that there is reasonable suppression of chloride interference down to a Cl^- : Hg^{++} ratio of about 1 : 5. Also there is not complete elimination even at a 1 : 20 ratio. That effective suppression is found in the automated system is extremely important. Whereas there could be loss of chloride by volatilisation in the manual procedure this is not open to the atmosphere during the heating stage. The mercury holds the chloride as soluble complex and mercury the excess of the amount required or complexing has no apparent effect. Unfortunately the solubility of the mercury (II) sulphate is limited in the strongly acid mixed solution. This is the limiting factor on how much chloride in a sample can be effectively suppressed.

5.12. SAFETY CUT-OUT DEVICE.

The low level system was tested for its suitability as a monitor system by leaving the system running for long unattended periods such as overnight and over the weekend. The overall performance was extremely mixed with some near disasters being recorded.

The major drawbacks continued to be connected with the need to pump the mixed solutions and base solution. The pumping was often erratic and tube failure occured fairly frequently. This often caused a build up of mixture in the mixing pot and eventual overflow of this very corrosive mixture. Blockage of the coil also caused blown joints with equally unpleasent results.

In order to overcome some of the unpleasent consequences of failure of the system a safety cut-out system was developed. This was a protective device which when triggered shut off the

electric supply to the entire system. Basically it consisted of two microswitches mounted one each end of the chart recorder scale. Should the recorder pen move offscale at either end a microswitch would be activated. Should the microswitch remain activated for the period of time set on an adjustable time clock the mains supply would be shut off. The recorder pen would normally be operating within the chart limits. If some malfunction occurred which caused air to enter the cell or if the cell became blocked recorder pen would shoot offscale and operate the cut-out. Pump tube failure, failure of the digestion solution dispenser, blowing of the connecting joints on the heating coil would all result in air entering the flow through cell. The system and associated circuit is described by Phillips. (85).

It became obvious during further trials that though the chemistry of the system worked well and the safety cutout system was successful, the system was insufficiently reliable for use as a long term unsupervised monitor. Further development was required to produce a system suitable for this purpose.

CHAPTER 6.

A COMPLETELY DISCRETE SYSTEM FOR COD. ANALYSIS

6.1. LAYOUT OF A MODIFIED SYSTEM.

Following the failure to achieve sufficient reliability of the part discrete/part continuous system during long unattended runs, consideration was given to modifying the system. Replacement of the peristaltic pump would produce a completely discrete system.

This could be achieved by using suction to draw the mixed solution from the mixing pot through the heating coils and then into the colorimeter flow cell. A second 'superspenser' dispenser would be very suitable for this purpose and could be easily wired into the existing cam timer. This superspenser would operate once per cycle shortly after the reagents and sample had been dispensed into the mixing pot. Figure B. shows the layout of the proposed system.

6.1.1. The long heating coil previously used to give sufficient residence time of the pumped stream in the heating bath is not required in the modified system. The heating time in the bath being dependent now on the cycle period chosen. The mixture from the mixing pot is sucked into a short heating coil in the heating bath by the first operation of the superspenser (C), and then out of the heating bath on the next operation of the superspenser (C). Therefore the heating period will be equal to the period between the two operations of this superspenser which is equivalent to the period of one cycle of the cam timer. Should the heating coil be equal to twice the take off volume of the superspenser (C).

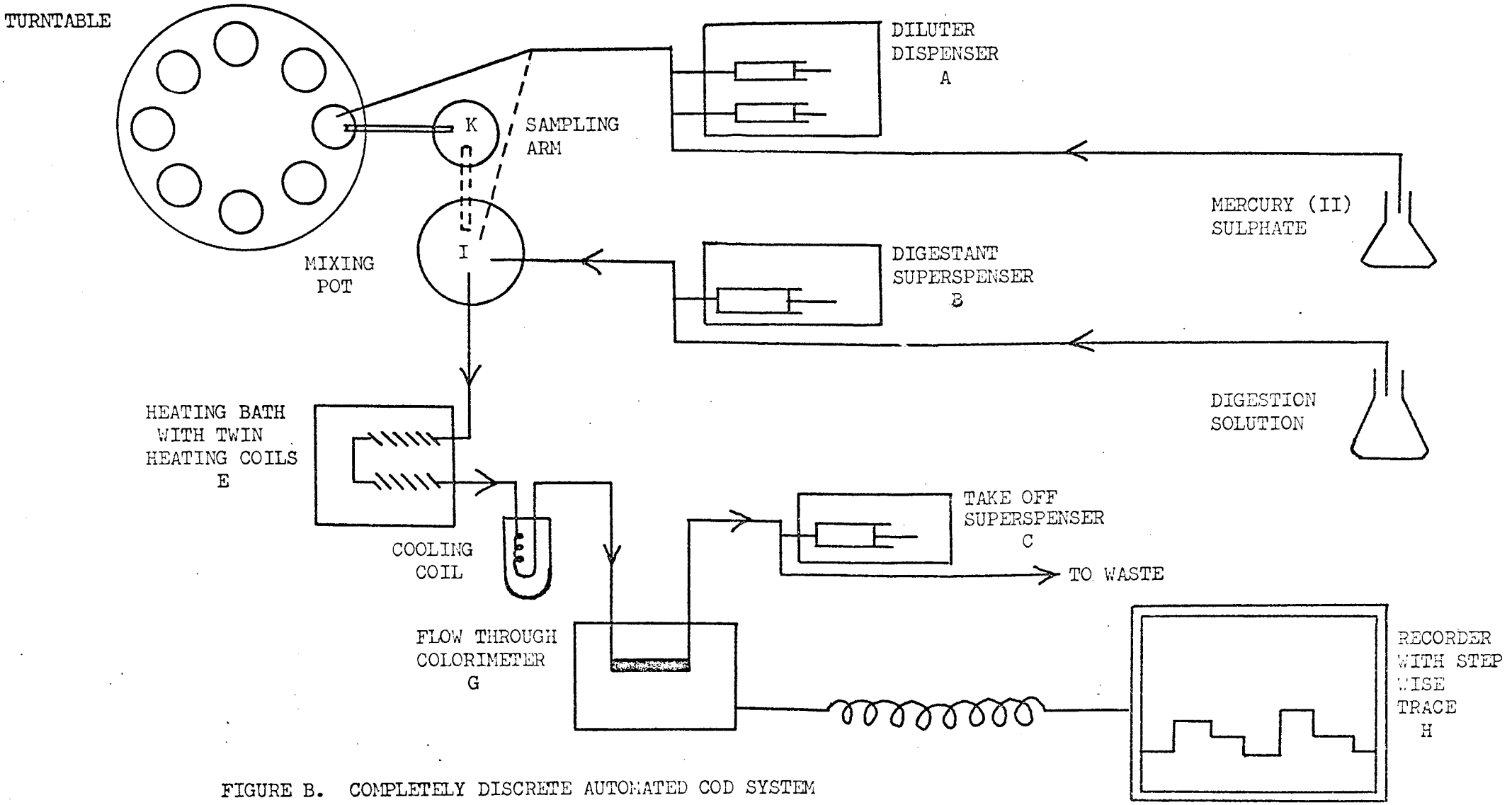


FIGURE B. COMPLETELY DISCRETE AUTOMATED COD SYSTEM

it will take two operations of the dispenser to remove the mixture from the heating coil. Therefore the heating period is double the time of one cycle of the cam timer. This reproducibility of heating period is preferable to the rather chancy heating period experienced with the pumped stream which varied as the pumping rate changed.

6.1.2. Connections between the mixing pot and heating coil, the coil and the Hellma flow through cell, and the Hellma cell and the superspenser (C), are made using 1 millimetre bore thin wall P.T.F.E. tubing. The P.T.F.E. tubing is normally connected to the various items by means of a short jointing sleeve of Viton fluorinated rubber tubing of 1.5 millimetre bore.

6.2. ASSEMBLY AND PRELIMINARY MODIFICATION OF THE PROPOSED SYSTEM

The modified system was assembled using a short length of glass helix of 2 millimetre bore holding a volume of about 9 ml., as the heating coil. The superspenser (C) was set to take up a volume about 0.5 ml. in excess of the total volume of the mixed solution. This allows a small amount of air to be drawn up into the P.T.F.E. tubing between the mixing pot and the coil, after the whole of the mixed solution had been sucked out of the mixing pot. This small amount of air creates an air gap between successive samples which considerably reduces the diffusion between successive samples.

6.2.1. The P.T.F.E. tubing between the heating coil and the flow cell was made long enough to hold about 3.0 ml. of the mixed solution. This ensures that the segment of the solution in the flow cell which will be measured, lies approximately two-thirds of the way along the length of the solution stream being pulled

through the coil and the colorimeter. This allows the first two-thirds of the stream to scavenge the residues of the previous solution left on the tubing and coil and minimises possible overlap.

6.2.2. The first time the system was operated the very high temperature of the solution pulled directly out of the heating bath into the flow cell caused it to crack open. In order to cool the solution before it enters the cell a section of the P.T.F.E. tubing between the heating coil and the flow cell was coiled inside a boiling tube, filled with water, stoppered by a rubber bung through which the P.T.F.E. tubing was led into and out of the boiling tube. Sufficient heat loss from the cooling water to the atmosphere occured to make it unnecessary to change the cooling water.

6.2.3. Initially the recorder was left switched on permanently. However, the recorder trace fluctuated so violently whenever a sample was being drawn through the cell that the procedure was altered. Instead the chart drive, which can be remotely switched, was linked to the cam timer to switch on for about one minute just before the next solution was drawn into the flow cell. This allows the solution in the cell a sufficient time lapse for it to adjust to the operating temperature of the colorimeter which is of the order of 34^{o}C. This helps to give a steady colour density reading and recorder trace. The event marker on the recorder was wired in parallel with the recorder switching cam to mark the chart each time the recorder switched on.

The recorder trace given appeared as a series of steps, each step equivalent to one sample. The COD. level being

deduced from the height of the step above a baseline step given by running distilled water in place of sample. The peak height of the unknown is referred to a calibration graph, drawn from the step height of known samples versus their COD. concentration in milligrams per litre.

6.3. PROGRAMME OF CYCLE OF OPERATIONS.

The sequence differed little from the sequence used for the previous part continuous part discrete system. There is however a fundamental difference concerning the period of heating. The previous system dpended on the pumping rate and coil volume to control the heating period which was independent of the time for a cycle to be completed. In the new system the heating period is a direct function of the cycle time and can be accurately controlled.

The sequence for the addition of sample, mercury (II) sulphate and digestion mixture to the mixing pot is unchanged. After mixing is complete the superspenser (C) operates. It completes an expel/intake cycle expelling any solution or air in the syringe to waste. On the intake stroke it provides the suction to pull the mixed solution from the mixing pot into the heating bath whilst moving the solution in the heating bath through the cooling tube and into the colorimeter. The next sample and reagents are dispensed into the mixing pot. Then about 2 minutes before the superspenser (C) again operates the cam timer switches the recorder drive on to record the signal from the colorimeter for one minute before switching off. This completes the cycle of operations.

The cycle time was chosen as 15 minutes. This appears to be adequate frequency for monitoring purposes based on the

expectation of only slow changes without violent fluctuations in the quality of final effluent discharged from a very large sewage works. Additionally, it was hoped that the 15 minute heating period would prove sufficient to achieve the desired degree of oxidation.

6.3.1. This system with a 15 minute heating period was found to give insufficient oxidation on final effluent samples, compared with the standard manual procedure generally in the order of 80%. It is possible that a pumped solution may receive greater oxidation in the same heating period than the same solution heated as a stationary slug lying inside the heating coils. If so, this is probably due to the pumped solution forming thin films of liquid over the heating coil where the air segments exist. These would receive a greater degree of heating than a solution filling the whole diameter of heating coil. Additionally, movement of the pumped solution could cause greater mixing and heat transfer than with the stationary solution.

To achieve more complete oxidation of the stationary solution either greater and/or longer heating is necessary. Greater heating could possibly lead to difficulties should the required increase be sufficient to cause the mixed solution to boil. This would require the acid concentration to be increased to raise the boiling point of the solution. Longer heating seems to present a better solution to the problem of insufficient oxidation. If the oxidation does proceed to a satisfactory extent the extra heating period then given would not substantially affect the result. That is unless an excessively high heating temperature caused excessive dichromate decomposition. In the manual procedures many samples are completely oxidised in an hour or less yet are left for the

two hours reflux period without any ill effect. The single coil system was therefore altered to a twin coil system. A pair of the new short coils were joined in series connected by fluorinated rubber tubing inside the fluidised heating bath. Instead of the mixed solution in the first heating coil being pulled into the colorimeter after its heating period, it is pulled into the second heating coil. It receives a greater heating period before it is pulled into the colorimeter. A heating period double the cycle period of the system is given which amounts to 30 minutes with the proposed system.

6.4. PERFORMANCE AND FURTHER MODIFICATIONS OF THE SYSTEM.

Initial results using the system showed good agreement with the manual procedure on samples of Minworth Works final effluent. Samples taken at varying times during the day gave results within the range 90% ± 10 of the manual procedure. This is a reasonable level of agreement when dealing with samples which are fairly low because the manual procedure itself will be subject to probably an error in the region of ± 5%. Additionally solids in the sample makes the sample non-homogeneous and more difficult to sample reproducibly.

6.4.1. Overlap between samples must be taken into account with the system. Running standards of known value in duplicate in random order established that there was an overlap of about 5% between successive samples. This means a result will be depressed or enhanced by the previous sample by 5% of the difference between the two results. This is of negligible consequence for on-stream monitoring where the difference between the successive samples will invariably be small.

6.4.2. Reproducibility of the system is dependent on two main

factors. Firstly the reproducibility of the colorimeter needs to be of a high order. The manufacturers claim an overall drift of less than 2% over 24 hours. In practice it was established that ambient temperature variation considerably increased this figure. During one experiment over 18 hours with a 12°C change in the ambient temperature, an overall drift in excess of 5% was recorded. With the pumped system previously used this was of little consequence as the base line was constantly being recorded between samples peaks. Therefore the sample peak height was easily measured. With the present system only the sample peak height was available the base line being periodically recorded by manual presentation to the pick-up probe of distilled water blanks. Therefore it becomes important to minimise the colorimeter drift as much as possible.

The second important factor on system reproducibility is the consistency of the volumes dispensed by the various automated dispensers. Over a 24 hour period analysing one standard in duplicate interspersed with duplicate water washes showed an accuracy of $\pm$ 2% of the mean value over the 24 hours. This confirms the reproducibility of the automated dispensers.

The effect of solids on reproducibility of analysis has already been mentioned. A sample of Minworth effluent was homogenised to disperse its solids, preserved with a small amount of 5% mercury (II) sulphate solution and analysed for 33 hours stirring vigorously all the time to ensure homogeneity. Duplicate water blanks were inserted as often as possible to establish the base line. The results showed that every result lay within the range 90 $\pm$ 6 milligrams per litre except for one result of 102 milligrams per litre. In contrast, replicate

analysis was carried out on a Minworth final effluent sample which had been settled and clean liquor partly decanted to increase the suspended solids content. The filtered and shaken, not homogenised, sample was analysed to show the effect of non-homogenised solids.

TABLE 18.

REPLICATE COD. RESULTS FOR FILTERED AND SHAKEN SAMPLES.

MILLIGRAMS PER LITRE COD.	
FILTERED SAMPLE	SHAKEN SAMPLE
93; 97; 94; 97; 94.	200; 185; 170; 190; 210.

It was obvious that the heavy solids were difficult to keep in suspension during sampling. Therefore the system must either incorporate some means of homogenising the sample or ensure by some means that the solids are kept freely suspended.

6.4.3. During the experiments with the system the actual volumes of sample, diluent and digestant as well as the volume pulled through the heating system were altered. However the ratios of the solutions remained the same. The volumes of some new glass coils were only about 6.5 ml, and a lot of interconnecting P.T.F.E. tubing was required to increase the volume sufficiently to accommodate the 10 ml. of mixed solution being used. The total volume of mixed solution was altered to 7.5 ml. and the volume of the take-off dispenser was set to 8.0 ml. This allowed an additional volume of 0.5 ml. of air to be taken as a buffer between the mixed solutions. Trouble was experienced with the

air gap because of its large expansion when in the heating bath. It became necessary to increase the P.T.F.E. tubing between the two coils to allow for the air expansion.

6.5. DETAILS OF THE SYSTEM USED FOR RELIABILITY TRIALS AND MODIFICATIONS FOUND NECESSARY.

The system evolved worked reasonably well and accurately for reliability trials over long periods to be next considered. The solutions and parameters now being used with the system were as follows:-

Mercury (II) sulphate diluent solution: 10 grams per litre mercury (II) sulphate solution in 5% v/v sulphuric acid.

Digestion solution: 0.6 grams per litre potassium dichromate, 0.6 grams per litre silver sulphate in 85% v/v sulphuric acid.

Volumes of solutions forming the mixed solution:

Sample 1.5 ml. diluent 0.5 ml. and digestion solution 5.5 ml.

Volume of take-off dispenser (C): 8.0 ml.

Flow cell 10 mm. path length

Temperature of fluidised heating bath - 155°C.

COD. range 0 - 300 mg/litre.

Colorimeter filter - 440 nanometres narrow band transmission filter.

Based on the work of Dobbs and Williams the amount of mercury (II) sulphate added is sufficient to suppress a sample chloride level of more than 250 milligrams per litre.

The trials consisted of running the system in the laboratory continuously to study its performance and observe the type of faults which could occur to see if they could be obviated or allowed for before installing on site. The sample was stored in a bird-bath

dispenser and was normally a solution of potassium hydrogen phthalate with a COD. value of 100 milligrams per litre.

6.5.1. A number of minor faults occured which it is possible to overcome by regular maintenance. Such things as the colorimeter bulb failing, the recorder ink ceasing to flow or running out. However, other faults appeared which required to be, as far as possible, eliminated.

6.5.2. The sampling arm carriage, which was controlled by micro switches at the end of its travel in both directions, showed a tendency to overrun on a number of occasions. The fault was very intermittent and continued to occur despite the repositioning of the micro switches, but to a much lesser extent.

6.5.3. There was constant trouble with superspensers both the one being used to dispense the digestion solution and the one used to pull through the mixed solution into the heating coil/colorimeter system. These dispensers work extremely well with aqueous and weakly acid or alkaline solutions but the highly viscous, strongly acid dichromate solutions are considerably more demanding on these dispensers. The dispensers employ a changeover valve on the intake/expel system which depend on two small O rings to create a seal as required. The syringe plunger also uses an O ring to form a leak-tight fit in the barrel of the syringe. It was necessary to use 'Viton' fluorinated rubber O rings for this work as the standard rubber O rings were rapidly attacked. The Viton O rings, though chemically stable, were machined to poor tolerance levels and swelled considerably upon prolonged contact with the acidic reagents. Therefore when an O ring capable of giving a good

seal was fitted subsequent swelling caused the fit to become extremely tight,often sufficient to cause seizure of the plunger in the barrel of the syringe. Allowing for the amount of swelling meant chancing a looser initial fit and possible leakage round the O rings. Both troubles occured quite frequently, more especially seizure due to swelling. This seizure has caused syringes to break and also pulled the syringe from its clamp. Subsequent acid spillage into the mechanism of the dispensers has been the most serious consequence. Electrical short circuiting normally occurs which is only a remote fire hazard, however the acid attack continues to cause damage until neutralized or removed.

Swelling of the small O rings in the changeover valves with subsequent seizure results in one port remaining open constantly, instead of the inlet and outlet ports being alternatively open and closed. Non-delivery of the required digestion solution volume resulted with the superspenser (B). Alternatively there is no take off of the mixed solution from the mixing pot through the heating system/colorimeter by the superspenser (C).

Seizure due to O rings swelling often occurs on a dispenser which has been out of use for long periods. It is frequently found after the system had been switched off over the weekend.

Since the first trials two alterations have considerably minimised some of the problems found with these dispensers. Firstly, the dispenser manufacturers changed the layout of the dispensers so that the syringe assembly and its associated mechanism lie side by side. Previously the syringe and changeover valve were directly above the mechanism. This considerably reduced spillage running into the mechanism. Prior to this modification appearing it had become common

practice to use the COD. system superspensers either upside down or on their side to minimise spillage effects. The second alteration was obtaining a supply of O rings from a different source which were of a better quality, and although subject to some swelling proved much superior for their purpose.

Experiments with P.T.F.E. O rings and plungers were tried, but a great deal of difficulty in maintaining a good seal led to their rejection.

6.5.4. Though oxidation seemed to be sufficient it was felt that better heating could be obtained by the use of coils with both a narrower bore and a thinner wall. Such coils would be considerably more vulnerable to breakage, but would normally be in the fluidised heating bath out of harms way. Coils were obtained from glass tubing of nominally 1.5 millimetres internal diameter and 2.0 millimetres outside diameter. The coils are approximately 100 millimetres in diameter having 12 to 14 turns. The only trouble with these narrow, fragile coils has been the difficulty of connecting the coils to the P.T.F.E. connecting tubing and to each other, without breaking them.

6.5.5. The air deliberately introduced into the system to separate the different samples showed itself to be a potential source of trouble. Its main drawback was the highly expanded volume it occupied when in the heating bath. Theoretically the system should set up an equilibrium. When the expanded air gap leaving the heating bath shows a rapid volume contraction it counteracts the rapid volume expansion of the new air gap entering the heating bath. In practice however, the sudden contractions and expansions resulted in the break-up of the air gap. Sometimes,

inexplicably, the position of the air gap would move progressively one way or other in the heating bath. The result was that the amount of uptake of sample and air varied from a fixed ratio. This sometimes meant solution was not completely removed from the mixing pot and mixed with the incoming sample causing contamination. Additionally, air sometimes filled the flow cell instead of solution giving an incorrect optical density measurement.

Drastically reducing the air volume intake was fairly successful but did not completely eliminate the problem which remained occasionally bothersome. It also increased overlap of samples but not to a significant extent.

6.5.6. Most of the possible failures attributable to the colorimeter/recorder system could be minimised by regular maintenance. However some electrical or mechanical failures are inevitable.

6.5.7. For a short period a 20 millimetre Hellma flow cell was used in the colorimeter in place of the usual 10 millimetre cell. This proved successful and gave a method of reducing the range of the system by a factor of two. This without having to increase the range expansion of the colorimeter, which is undesirable for long term stability, or to alter the dichromate concentration of the digestant solution. This last step would probably have little effect on results but would require experimental verification.

6.5.8. The temperature controller purchased with the fluidised sand bath suffered relay failure on several occasions. This presented no physical danger as the system has a fail safe arrangement, but meant that the heating bath ceased to operate and sample results were invalid. Basically the controller was

too sensitive for the particular long term needs of this COD. system. A less sensitive system would reduce the mechanical switching wear on the relays without impairing the accuracy of the overall system by any measurable amount.

6.6. A LABORATORY BASED COD. SYSTEM FOR ANALYSIS OF DISCRETE SAMPLES.

Attention was turned to experimenting with the proposed monitoring system just described, to test its usefulness as a laboratory based system for automated analysis of discrete samples. By discrete samples is meant the samples received in bottles by the laboratory for analysis; these fall into two categories.

One category consists of sewage works samples, river samples and samples from experimental research in the field of sewage treatment. The COD. range is quite wide ranging from the order of 20 milligrams per litre for clean river samples, to several thousand for raw sewage with excessive levels of solids. Normally it is possible to predict the approximate range of a sample from its appearance and source except occasionally for samples contaminated by trade waste discharge.

The second category covers samples of trade effluents discharged into the public sewers taken for control and charging purposes. It is difficult to predict the COD. levels of these samples without a great deal of background knowledge and experience. It is amazing how close an experienced operator can guess the value of a sample especially when the source of the sample is only one of more than two thousand. The range of COD. values is extremely wide ranging from negative values

to several million quoted as milligrams per litre. These high figures are not merely hypothetical as samples have been submitted having COD. values in excess of one million milligrams per litre.

The on-stream system using a 15 minute cycle period is too slow for the required throughput of samples. In a normal working day the number of samples analysed could not exceed 25 per day. The numbers envisaged would be in excess of treble this number including blanks and standards necessary for calibration purposes.

The system required to be modified as little as possible but with a sampling rate more than double the proposed monitoring rate of 4 times per hour.

The system devised was based on a cycle time of 5 or 6 minutes giving a sampling rate of 10 or 12 samples per hour. To ensure an adequate heating period 4 coils were incorporated into the system instead of the two previously used.

6.6.1. Initially the 4 coils were joined in series. This meant every sample went through all 4 coils, one after the other, spending a period equivalent to 1 cycle period in each. The actual heating period for each sample was either 20 or 24 minutes dependent on whether a 5 or 6 minute cycle was used. This system was abandoned because of the enhanced sample overlap together with the trouble caused by introducing another 2 air gaps into the heating bath. The additional strain imposed by the extra mixed solution on the pull through dispenser (C) was also undesirable.

Instead the 4 coils were split into pairs, one pair in parallel with the other pair. Each pair of coils is connected at one end to the mixing pot. At the other end one pair is connected to one inlet port of a motorised two-way valve, and

the other pair is connected to the second inlet port of the valve. The common exit port of the valve is connected to the cooling tube, colorimeter and intake of superspenser (C). exactly as for the monitoring system. Figure C. shows the layout of the system. The motorised valve has one inlet port open and the other closed as its normal mode and it changes over on a signal from the cam timer once during each cycle. The analytical cycle is exactly as described for the on-stream system except that sequential mixed solutions from the mixing pot are drawn into alternative pairs of coils. Each individual mixed solution receives a heating period equivalent to two cycle periods in both the first and second coils of one or other of the pairs, giving a total heating period of 4 times the cycle period.

6.6.2. The system worked well leaving the question of the cycle period and temperature to be decided.

The 5 minute cycle period could not be altered greatly. A much shorter period would require increased temperature beyond the boiling point of the mixture, which would itself then require modification, or the possible addition of a third coil in the system with its attendant problems. A much extended cycle period would on the other hand reduce sample throughput below a reasonable level. The temperature could be varied but again criteria existed as to the amount of variation. The lowest temperature usable would not sensibly be less than the temperature of 155°C. used in the proposed on-stream monitoring system. The higher temperature is theoretically dependent only on the boiling point of the mixed solution which is in turn dependent on the acid concentration of the mixture. In practical terms the upper limit would be in the order of 175°C, based on the

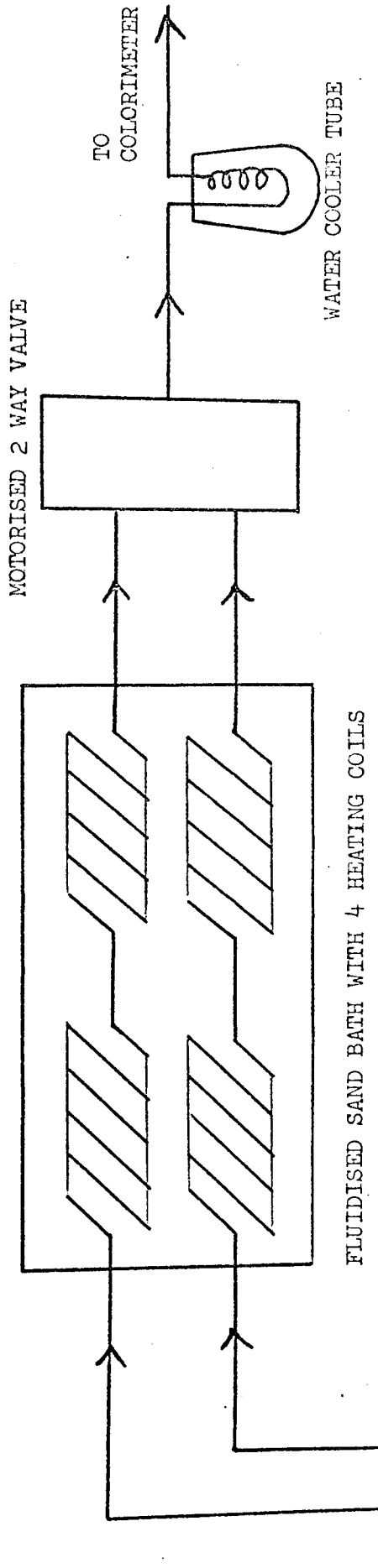


FIGURE C. TWIN HEATING SYSTEM FOR LABORATORY COD SYSTEM.

difficulty of handling the higher acid solutions and probable excessive breakdown of dichromate at very high temperatures.

An evaluation programme, based on combinations of cycle periods of 5 and 6 minutes and temperatures ranging between 155 and 175°C, was carried out on sewage works samples. These ranged from crude sewage to final effluents from tertiary treatment. The COD. of most samples examined would lie in the range 50 to 700 milligrams per litre. Therefore the potassium dichromate concentration in the digestion solution was raised from 0.6 grams to 1.5 grams per litre to cover this range. The sulphuric acid concentration of the digestion solution was also raised from 85% to 90% v/v to raise the boiling point of the mixed solution to accommodate any increase in the heating bath temperature.

6.6.3. Previous work had shown the necessity of homogenising samples containing suspended solids. Initially it had been planned to homogenise the sample in bulk and then transfer to 2.0 millilitre polystyrene sample cups on the sample turntable. Suspended solids would settle while standing on the turntable. However, it was thought blowing a stream of air bubbles into the sample through the sample pick-up probe prior to pick-up would re-suspend the solids homogeneously. The sample air blowing was achieved by simply extending the period of air blowing used to create the anti diffusion air gap in the sample probe, as described in 5.7.4. The air used was bled off the purifed air being blown into the mixing pot via a motorised valve controlled from the cam timer. The air stream was programmed to start just after sample ejection into the mixing pot and cease about 10 seconds before sample uptake.

Visual observation showed that the samples with high suspended

solids were insufficiently mixed using this system. The reason being the layer of solids on the bottom of the cup could not be reached by the air bubbles with sufficient force to break up the layer.

Automated homogenising as part of the analytical cycle was therefore introduced. Instead of a 2 ml. sample cup, the sample was placed in a much larger polystyrene disposable cup holding about 25 ml. These were placed on a modified turntable top capable of holding these larger cups. A stainless steel rod of approximately 10 millimetres diameter, had several angled grooves cut into the bottom few inches of the rod, to provide cutting edges, and was placed in a fixed position two inches above the sample cup. This homogeniser blade was driven by a small electric motor controlled by a cam on the cam timer. The sample cup about to be sampled was lifted upwards on a lifting platform. This was based on an eccentric cam, driven by a slow-running electric motor controlled at the maximum and minimum lift positions by micro switches. These positions would be held until a signal from the cam timer caused the lift to raise or lower as appropriate. Both the sampling probe and homogeniser blade became immersed in the sample when the sample cup was lifted. The sample was homogenised and sampled immediately after homogenisation ceased. The sample cup was lowered back onto the turntable which then moved the next sample into the lifting position.

The solenoid incorporated in the sampling arm, to allow the probe to drop into and lift out of the sample cup, was no longer required using the new cup lifting system. The sampling arm, which had previously given some mechanical trouble, was replaced. Instead a simpler system in lightweight aluminium consisting of

an arm, which travelled only in a horizontal plane between sampling position and mixing pot, driven by a small reversible electric motor, was used.

6.7. RESULTS FOR VARIOUS TEMPERATURE/HEATING TIME COMBINATIONS.

Preliminary tests soon indicated that samples required only a short homogenisation period. Sufficient homogeneity was produced by homogenising for 20 to 30 seconds at a speed of 2,500 r.p.m. which is half the maximum speed of the homogeniser motor. Successive homogenising of the same sample or an extended period of homogenising caused a steady reduction in the COD. figure initially found, possibly attributable to loss of volatile organic matter. This reduction was more pronounced the cruder the sample.

6.7.1. Two different crude sewages were analysed by the automated system using a 5 minutes cycle period and a heating temperature of 160°C. Before placing in the sample cup a large volume of the sample was homogenised for 30 seconds at 5,000 r.p.m. to ensure each sample cup held identical samples. A portion of the homogenised bulk sample was also diluted with an equal volume of distilled water, and the diluted sample also analysed by the same procedure. A sample of the diluted sewage was analysed by the standard manual procedure.

The reproducibility of the system was tested by filling a number of sample cups simultaneously from a well shaken bottle of the sample and running them successively through the system, using a 30 second homogenising period at 2,500 r.p.m.

The results, shown in Table 20, indicate that reproducability is enhanced by homogenising the sample. Homogenising would however, seem to be responsible for some reduction in COD.

TABLE 19

AUTOMATED ANALYSIS USING TWENTY MINUTES HEATING AT 160°C

SAMPLE	SPEED OF HOMOGENISER (R.P.M.)	HOMOGENISING TIME IN SECONDS	SAMPLE DILUTION	COD IN MILLIGRAMS PER LITRE	
				AUTOMATED PROCEDURE	MANUAL PROCEDURE
A	2,500	30	-	690	
	2,500	30	-	660	
	2,500	30	-	690	
	nil	nil	-	725	
	nil	nil	-	725	
	2,500	30	x2	300	
	2,500	30	x2	310	
	nil	nil	x2	340	307
B	2,500	30	-	600	
	2,500	30	-	620	
	2,500	30	-	590	
	2,500	30	x2	300	286
	2,500	30	x2	275	

TABLE 20.

REPRODUCIBILITY OF AUTOMATED RESULTS USING 20 MINUTES HEATING AT 160°C.

SAMPLE	INDIVIDUAL COD. RESULTS IN MILLIGRAMS PER LITRE
Crude Sewage	525, 530, 570
Primary sedimented sewage	365, 375, 365, 375
Final effluent	85, 105, 95, 105

6.7.2. The effect of higher heating bath temperatures was tried out by raising the bath temperature to 175°C using the 5 minute cycle period. Each sample being analysed in replicate. Each sample was also analysed by the standard British macro manual procedure. The results found are shown in Table 21.

The conclusion to be reached from the results in Table 21 was that the cruder samples, containing a large proportion of easier to oxidise organic material, gave excellent agreement between the two analytical procedures. The clean samples obviously contain a large proportion of the more resistant to oxidation material. The conclusion reached, from the markedly higher COD. results given by the automated procedure, was that it gave more severe oxidation conditions than the manual procedure.

6.7.3. To measure the reduction in the severity of oxidation by a temperature reduction of the heating bath, samples were run in replicate at both 165°C and 175°C. The samples used were mainly final effluent samples which would be expected to show the biggest percentage change in COD. value. Table 22. shows

TABLE 21

AUTOMATED ANALYSIS USING TWENTY MINUTES HEATING AT 175°C

SAMPLE	COD IN MILLIGRAMS PER LITRE	
	AUTOMATED PROCEDURE	MANUAL PROCEDURE
Sedimented Sewage (Worksa A)	300; 300; 310; 290;	290
Filter Bed Effluent (Works A)	360; 380; 370; 350;	380
Final Effluent (Works A)	165; 155; 165; 145;	105
Sedimented Sewage (Works B)	485; 515; 515; 550; 495;	550
Final effluent (Works B)	175; 175; 160; 185;	82
Crude Sewage (Works C)	260; 260; 250; 240; 230;	260
Final Effluent (Works C)	110; 120; 110; 110;	60
Sedimented Sewage (Works D)	445; 460; 460; 430;	450
Final Effluent (Works D)	130; 120; 110;	150
Sedimented Sewage (Works E)	380; 400; 420; 400;	410
Filter Bed Effluent (Works E)	310; 300; 290; 240;	165
Humus Tank Effluent (Works E)	130; 110; 130;	95
Grass Plot Effluent (Works E)	90; 100; 70; 70;	70

the results found at the two temperatures also the value found by the manual procedure.

The table shows that much more satisfactory agreement with the manual procedure results from using a temperature of 165°C. Even so, in many cases the results are still higher than the manual procedure. This is particularly noticeable with the very clean samples such as grass plot effluents while humus effluents, which differ mainly in containing more suspended solids, show reasonable agreement. The inference is that the soluble organics are difficult to oxidise while the suspended organic solids are more easily oxidised and contribute substantially to the COD. content of a sample.

6.7.4. The effect of varying the reaction temperature on the COD. figure of cruder samples was next investigated. Initially only 165°C and 175°C were used but later some samples were also analysed at 170°C.

Table 23 indicates the results found at the different temperatures.

All the crude sewages were diluted with an equal volume of distilled water before analysis. The very variable suspended solids levels in crude sewage were responsible for the wide variation in the COD. level.

The results support the conclusion that crude samples contain such a high proportion of easily oxidised material that any of the temperatures used give good agreement with the manual procedure results. It can also be seen that there is some loss upon homogenisation for the initial result is nearly always the

TABLE 22

COMPARISON OF THE SEVERITY OF OXIDATION IN THE AUTOMATED PROCEDURE

SHAKEN SAMPLE	WORKS	COD IN MILLIGRAMS PER LITRE		
		AUTOMATED PROCEDURE		MANUAL PROCEDURE
		165°C	175°C	
Final Effluent	A	65; 75; 65; 70;	85; 75;	65
Final Effluent	B	125; 155; 145; 125;	170; 160;	110
Final Effluent	C	170; 170; 170; 160;	215; 170;	140
Final Effluent	A	45; 55;	75; 75;	55
Final Effluent	D	90; 90;	110; 110; 110;	115; 120;
Grass Plot Effluent	E	70; 80;	80; 80; 80;	45
Humus Effluent	E	90; 90;	105; 105;	90
Final Effluent	F	80; 80; 70;	95; 80; 80;	60
Grass Plot Effluent	G	60; 60; 40;	80; 80; 80;	45
Humus Effluent	G	70; 80; 80;	95; 95; 95;	75
Final Effluent	H	60; 60;	95; 95;	70; 65;
Final Effluent	I	90; 90;	125;	100

TABLE 23

COMPARISON OF AUTOMATED PROCEDURE RESULTS ON CRUDE SAMPLES AT DIFFERENT TEMPERATURES

SHAKEN SAMPLE	WORKS	COD IN MILLIGRAMS PER LITRE			
		AUTOMATED PROCEDURE			MANUAL PROCEDURE
		165°C	170°C	175°C	
Sedimented Sewage	A	500; 485; 485		465; 455	515
Sedimented Sewage	B	125; 135; 125		130; 110;	125
Crude Sewage	C	210; 220; 220		235; 235; 250	230
Crude Sewage	D	260; 260; 240		250; 260; 260	300
Crude Sewage	E	230; 200; 180		215; 195; 205	235
Crude Sewage	F	335; 285; 265		250; 250;	345
Crude Sewage	G	265; 255		330	280
Crude Sewage	H	210; 190; 170	220; 210; 200	185; 185; 185	225; 140
Crude Sewage	H	715; 700	620; 600	500; 520;	675
Sedimented Sewage	H	520; 480	490; 490	470; 470;	455
Sedimented Sewage	H	310; 290; 290	325; 315; 320	330; 340; 330	345; 350
Crude Sewage	I	225; 205; 205	195; 195; 185	215; 215; 215	230
Sedimented Sewage	I	295; 275	275; 265	300; 290	270
Crude Sewage	D	400; 410; 370	415; 405	350; 320	420
Sedimented Sewage	D	250; 250	270; 250	260; 250	250

highest and the subsequent homogenisations show little or no loss due to volatilisation.

6.7.5. The cycle period of the procedure was increased from 5 to 6 minutes for trial purposes. This increased the total heating period for each sample from 20 minutes to 24 minutes. The cleaner sewage works samples were analysed initially at heating temperatures of 160°and 170°C and later also at 150°C.

Results show that 150°C gives the best agreement with the manual procedure but even so produces greater oxidation, in many cases, than the manual procedure. At COD. levels below 100 milligrams per litre the accuracy of the manual procedure begins to suffer because of the small amount of dichromate consumed. This is not very easy to measure with great accuracy, and is also unduly influenced by any small variation in the method blank value. This must influence the agreement between different methods, and caution must be taken in any assessment.

Some cruder samples were analysed using the extended reaction time at the three temperatures used previously. The results are shown in Table 25.

The good agreement between the results at varying temperatures shows that any of the temperatures should be capable of being used with reasonable expectancy of good agreement with the manual procedure results.

6.7.6. Hourly samples taken from a number of points on the River Tame during a survey were analysed for COD. value. The samples were analysed using the automated procedure

TABLE 24

COMPARATIVE AUTOMATED COD VALUES AT VARIOUS TEMPERATURES USING A 24 MINUTES HEATING PERIOD

SHAKEN SAMPLE	WORKS	COD IN MILLIGRAMS PER LITRE			
		AUTOMATED PROCEDURE			MANUAL PROCEDURE
		150°C	160°C	170°C	
Humus Effluent	A		145; 135	175; 175	110
Humus Effluent	B		90; 75	105; 95	85
Humus Effluent	C		90; 75	105	65
Bacteria Bed Effluent	D	100; 80	110; 110	155; 145	85
Humus Effluent	D	70; 60	65; 90	110; 90	70
Grass Plot Effluent	E	50; 50	65; 65	90; 80	50
Bacteria Bed Effluent	F	125; 115; 115	155; 155		85
Humus Effluent	F	85; 75	95; 95		70
Grass Plot Effluent	F	65; 65	75; 75		50
Humus Effluent	G	165; 155	165; 165		165
Final Effluent	H	90; 90			70

TABLE 25

COMPARATIVE AUTOMATED COD VALUES USING EXTENDED HEATING AT VARIOUS TEMPERATURES FOR CRUDE SEWAGE SAMPLES

SHAKEN SAMPLE	WORKS	COD IN MILLIGRAMS PER LITRE			
		AUTOMATED PROCEDURE			MANUAL PROCEDURE
		150°C	160°C	170°C	
Crude Sewage	A		295; 305	300; 290	320
Sedimented Sewage	A		325; 305	345; 325	300
Bacteria Bed Effluent	A		175; 155	220; 215	120
Crude Sewage	B		370; 360	380; 350	375
Sedimented Sewage	B		500; 490	540; 520	520
Crude Sewage	C		305; 285	300; 280	270
Sedimented Sewage	C	185; 165	190; 190	220; 210	175
Crude Sewage	E	540; 540	535; 510	510; 520	520
Sedimented Sewage	F	530; 530			525
Crude Sewage	G	710; 710	680; 715		730
Sedimented Sewage	G	505; 470	490; 490		468
Crude Sewage	H	520; 520			560
Sedimented Sewage	H	390; 400			445

because of insufficient capacity for manual analysis which was confined to checking every tenth sample. Because of its polluted state the river would have higher COD. values than most rivers. It would be expected however to contain mostly difficult to oxidise material and therefore the system was set to operate with a 5 minute cycle period using a temperature of 160°C. In addition the COD. range was reduced, using the amplification system of the colorimeter, to give greater accuracy of the samples which would all be expected to be relatively low. Table 26 shows only the samples which were also analysed by the manual procedure.

6.7.7. There are a number of conclusions to be gathered from the results found using various combinations of temperature and heating time in the automated procedure.

It is possible to use a number of different combinations of time and temperature and obtain reasonable agreement, with the manual procedure, for crude or poorly purified samples. This is because the large proportion of easily oxidisable organic material masks the variation in the relative severity of the various combinations used.

Conversely, the cleaner or more purified a sample is the greater becomes the variation between the results obtained by varying the parameters of time and temperature. One of the most puzzling facts is that considerably higher COD. values can be obtained with clean samples, using a 20 minutes heating period at temperatures exceeding 165°C, than with the manual procedure. The manual procedure having a 2 hours heating period at a reflux temperature of approximately 148°C. It could be that

TABLE 26

COD VALUES FOR RIVER TAME SAMPLES
USING BOTH MANUAL AND AUTOMATED PROCEDURES

SAMPLING POSITION	COD IN MILLIGRAMS PER LITRE	
	AUTOMATED PROCEDURE	MANUAL PROCEDURE
1	170	205
1	125	115
1	100	110
2	245	240
2	130	135
2	145	145
2	90	125
3	80	70
3	105	75
3	70	75
3	95	80
4	90	100
4	70	75
4	70	65
4	65	65
5	210	210
5	70	110
5	60	50
5	70	70
6	235	230
6	105	105
6	190	215
6	70	95
7	150	120
7	110	105
7	90	75
8	190	210
8	95	90
3	105	110

there is a greater loss in volatiles with the open reflux system, than with the automated procedure which is a closed heating system. It could equally be that the really important parameter is temperature and not time. There is little doubt there is residual organic material which is difficult to oxidise in purified sewage works' discharges. These may respond to a higher oxidising temperature but not to an increase in the heating period.

The problem of loss of volatiles on sample pretreatment is more serious with the cruder samples than with treated samples.

6.8. PARAMETERS FOR AUTOMATED ANALYSIS OF TRADE EFFLUENT SAMPLES.

The most suitable parameters for analysis of sewage works samples seem to vary with the sample source. The parameters chosen as most suitable for all types of sewage works' samples was a 20 minute heating period coupled with a temperature of 165°C or alternatively, 24 minutes at 160°C. In fact, a compromise of these alternatives, 20 minutes at 160°C was chosen for trials on trade effluent samples.

The problem of determining COD. values of trade effluents is large and complex for a sewage treatment authority embracing a highly industrialised area, such as exists in the West Midlands area. The Upper Tame Main Drainage Authority received into its sewage treatment works over two thousand separate trade effluent discharges. The volume and types of discharge vary enormously and covers almost every type of industrial waste.

There were two basic decisions established as guide lines before the commencement of the use of the COD. value for trade effluent control and treatment charging purposes. One was that

the analysis would be carried out on the supernatant liquor of the sample, after quiescent standing for a minimum of one hour. This avoids a double charge on suspended solids, which are controlled and charged for as a separate item. The second decision was that all trade effluents, without exception, would be analysed for their COD. content. This involved totals of the order of 20,000 to 25,000 samples per year or 80 to 100 samples per working day.

The only possible way to check that there is true agreement between the manual and the automated procedures is to analyse every sample received every time. Instead samples chosen at random were analysed by the two procedures. The agreement was good and taken in conjunction with the good agreement shown in tables, 12, 13, 14 and 15 was sufficient to adopt the automated procedure as a screening system in the first instance. The position to be reviewed after studying the agreement found in the long term. The procedure adopted was to run all samples which were thought to be less than 250 mg/l by the automated procedure. Then analysing any found to be greater than 100 milligrams per litre COD. by the manual procedure.

Although it is a sweeping statement experience indicates that most trade effluents contain easily oxidisable material which allows good percentage agreement with oxidising conditions of varying severity. If this is correct good agreement between automated and manual analysis will be the normal case especially when non-homogeneity is avoided by the use of settled samples. This assumption discounts the probably substantial effect of experimental error with samples of low COD. values.

6.9. GENERAL CONCLUSION ON THE COMPLETELY DISCRETE AUTOMATED COD. SYSTEM.

The conclusion reached was that the system developed showed sufficient promise to be extensively tested for both monitoring and discrete analysis purposes.

The monitoring system would probably require further development to improve reliability, but the chemistry would probably be good enough because only one kind of sample would be involved.

The laboratory discrete analyser would also obviously benefit from improved reliability. Being laboratory based however reliability is of lesser importance than having good analytical agreement with the manual method. The range used experimentally had been selected as 0 - 600 milligrams per litre COD. for trade effluents. Preliminary COD. figures for trade effluents indicate that a much shorter COD. range up to 250 or 300 milligrams per litre would be more suitable. Not only would the large majority of settled trade effluents be covered by this range, but there would be a proportionate increase in accuracy.

CHAPTER 7.

EXPERIENCE FOUND USING COMPLETELY DISCRETE AUTOMATED COD. ANALYZERS.

The experience of using the automated system on stream and as a laboratory analyzer is discussed. The initial steps involved installing the system in a monitoring station and testing the system over a long period. The second step was the fabrication of a laboratory based system for analysis of discrete samples. The installation and subsequent experience with both instruments is described.

7.1. THE INSTALLATION OF THE SYSTEM AS AN ON-STREAM MONITOR.

As indicated previously the intention in designing the system included its use as a monitor of the oxygen demand value, in the form of a COD. determination, of the final effluents discharged from a major sewage works.

So much trouble was given by the O rings in the two dispensers handling the highly acidic mixture in the period before installation of the instrument, that it made the success of using it on-steam very doubtful.

The provision of a better quality, more uniform O ring resulted in the decision to proceed with the installation. These new O rings were still not really good enough for the purpose required, but in view of the fact that the monitoring hut would be inspected each day it was felt the risk of failure would be justified for the information that might be gained. This decision was reinforced by the incorporation of the

automatic safety cut out system described in 5.1.2. which afforded a considerable measure of protection when faults occured. The safety system was so wired that it could be switched into or out of operation as required. The built in time delay before the cut out operated was set at 30 seconds initially.

7.1.1. The system installed in the monitoring hut was very makeshift, merely assembling the various units as conveniently as possible in a very limited amount of space. It was set up with a 15 minute cycle period utilising two heating coils to give a 30 minute heating period at a heating bath temperature of 155°C.

The range was set from 0 to 300 milligrams per litre COD. using a 20 millimeter path length flow cell and a wavelength of 440 nanometers with the colorimeter. The volumes added to the mixing pot were 1.2 millilitre of sample, 0.8 millilitres of 1% mercury (II) sulphate in 5% sulphuric acid as the sample diluent, and 6.0 millilitres of digestion solution. The digestion solution contained 0.6 grams per litre of potassium dichromate, 6.0 grams per litre of silver sulphate and it was approximately 85% v/v with respect to sulphuric acid.

7.1.2. The monitoring hut is a 6' x 6' brick building fitted with mains electricity. Space was limited because other monitoring equipment had also been installed. The hut is situated alongside the channel carrying the final effluent from the bacteria beds at the sewage disposal works at Minworth, Warwickshire.

A 10 gallon per minute mono pump is used to pump the effluent through a 2 inch ring main in the hut and then to waste. The ring main has a number of tapped outlets to allow take off of

the pumped effluent as required.

The supply for the COD. sample was made by feeding the effluent from one of the ring main valves via rubber tubing to a three litre rigid unplasticised polythene bottle. The base of the bottle was cut off and the bottle mounted in an upsidedown position. The effluent supply was fed into the bottle at a force sufficient to hold the suspended solids in suspension. It was necessary, because the redesigned sampling arm no longer had a dip and lift action incorporated, to cut a vee notch in the top of the plastic bottle to allow the sampling probe to swing into this sampling source below the level of the sample surface.

The use of four vee notches cut about 10 millimetres deep formed a good system for overflowing the sample out of the bottle without creating much turbulence. In the centre of the bottle was a smooth well mixed spot, the level being sufficiently above the vee notches to ensure the sampling probe was always immersed in the sample.

7.1.3. The apparatus was run for a period of six weeks before serious electrical interference made it impossible to use. This was caused by the Minworth Works switching from the use of the Midland Electricity Board electrical supply to a self generated supply. This new supply was perfectly adequate for works operation, but proved unsuitable for some important items of the COD. system in particular the colorimeter and recorder. The large voltage fluctuations in the supply was not the problem as the voltage stabilising units in the system could normally cope with these fluctuations. Of much greater consequence was

the fluctuation in frequency which was considerably in excess of the fluctuations specified for public supply. Attempts were made to maintain a better frequency control. Because of the relatively small amount of electricity produced compared with the public supply, the required control was impossible to maintain.

Attempts were then made to stabilize the frequency of the supply in the monitoring hut by continuously charging two 24 volt heavy duty batteries in series, so giving a stable 24 volt D.C. supply. This was fed into a commercial power pack capable of converting it to a stable 240 volt, 50 Hertz output. The system worked well when only a small demand was made on the stabilized supply. However the COD. system demand was such that a heavy drain was created on the two batteries. This turn required such a heavy charging rate, that the D.C. supply from the batteries was found to have a sufficiently high A.C. component superimposed that some transistors in the power pack were destroyed.

A commercial D.C. power pack gave a sufficiently high D.C. supply, without the A.C. component for the required stabilized A.C. supply. Unfortunately, within a short period of time the transverter in this D.C. power pack ceased to work.

The faults and delays associated with obtaining equipment and replacements from manufacturers caused an extensive delay. The commencement of works extensions meant electricity board mains power would again become available in the monitoring hut at some future date. It was therefore decided to await this reinstallation before re-using the COD. monitoring system.

7.2. REFURBISHING OF THE AUTOMATED SYSTEM.

The opportunity was taken during the period before re-installation of mains electricity to tidy up the system by installing most of the controls and wiring into a console unit. From the rear of the console ran cables to each of the individual items. The cam timer was bolted onto the side of the console to allow easy access. Both the temperature controller and the time delay clock of the automatic safety cut-out, were also wired into the console with their adjustable dial faces fitted into the front panel of the console. This allows easy modification of the temperature or time delay to be made. Additionally the mains on/off switch, the cam timer on/off switch, and the switch for switching the safety cut-out in or out of circuit, were also mounted on the front panel. Push buttons to activate the sampling arm, dispensers, and the change over valve independent of the cam timer were also fitted. Photograph 1. in the appendix shows the completed console.

7.2.1. During the delay period the necessary apparatus was also collected for a laboratory based instrument which was also constructed using a central control console. The two instruments were purposely kept as similar as possible though the laboratory based system also required a turntable, a twin set of heating coils, and a two way valve to switch the stream path. It was decided for the present to keep the reagent strengths, the volumes dispensed and the COD. range measured, the same for both systems.

7.2.2. The on-stream system possessed no means of giving a periodic check reading to indicate that the system had functioned correctly, during the periods between check visits to the monitoring hut.

It is desirable that such a check should be incorporated into the system. A system was therefore devised for substituting a standard of known value in place of the sample approximately every three hours, and this was incorporated in the refurbished monitoring system.

The device was based on a contact set containing 13 separate sets of contact. A wiper blade shorted out each separate set of contacts sequentially moving on to the next when given an external signal. The contact set was wired to the cam timer which gave one signal per revolution. Therefore, the wiper blade wiped all thirteen contacts in a period of three hours fifteen minutes. One of the sets of contacts is wired to a relay which when shorted by the wiper blade de-energises the diluter-dispenser so that no sample is dispensed. Simultaneously the relay energises a separate dispenser, which delivers a volume of potassium hydrogen phthalate standard of known strength equal to the volume normally dispensed by the diluter dispenser. Therefore, every thirteenth cycle a standard is measured by the system instead of a sample.

7.3. THE PERFORMANCE OF THE ON-STREAMMONITOR SYSTEM.

The rebuilt system was replaced in the monitoring hut in January 1971 the electricity board supply having been re-connected. A description of the performance over extended usage is given as a monthly summary for the first six months, followed by a general conclusion covering a much longer period.

7.3.1. Three faults caused breakdown during the month of January. The first was due to the take off superspenser (C) jamming, because of an excessively swollen O ring. This fault did not cause the cut-out safety system to operate, therefore, sample

and digestion solution continued to be dispensed causing the mixing pot to overflow. The spillage ran to waste via a funnel placed beneath the mixing pot for just such an emergency. The system did switch off however when mercury (II) sulphate came out of the solution during extended residence in the flow cell and the associated tubing. The gradual build up of precipitated mercury (II) sulphate in the system after the cooling tube, particularly in the flow cell, is very undesirable. Because the Minworth final effluent chloride content never exceeds 150 milligrams per litre it was decided to reduce the strength of mercury (II) sulphate solution added to the sample. The concentration was halved from 1% to 0.5% w/v, which is still capable of suppressing chloride levels in samples in excess of 250 milligrams per litre, based on the results shown in Table 17. The third fault was the failure of the motor chopping the light beam in the colorimeter to produce an A.C. signal. This fault has only ever occured once and illustrates the virtual impossibility of anticipating all possible faults.

7.3.2. In February there was a minor breakdown due to a blown fuse. The main trouble occured because of an intermittent fault. This proved difficult to trace and was finally found due to one of the cams on the cam timer slipping, allowing the digestion solution dispenser to occasionally fire twice per cycle.

It was during this period it was discovered that the digestion mixture was being reduced by the action of light to a significant extent. Over a period of time it was found that although initially the digestant was made strong enough to oxidise samples up to a COD. strength of 300 milligrams per

litre, after several days the digestant was exhausted by samples well below this level. Two volumes of the same digestion solution one in a clear, and one in a brown bottle, were stoppered and stood in the open laboratory. Titrations with iron (II) ammonium sulphate solutions showed a daily decline in the case of the clear bottled solution while the amber bottled solution showed no decrease in oxidation strength when stood in the dark.

The total period out of use during February was about 40 hours.

7.3.3. In March about 3 days were lost when the clutch mechanism of the recorder malfunctioned and required replacing. This was another example of an unforeseen breakdown.

7.3.4. The apparatus worked well during April but unfortunately the monitoring hut was vandalised. Although the apparatus was untouched the tubing taking the sample in and out of the hut was stolen and required replacing before monitoring could be resumed.

7.3.5. The apparatus hardly worked at all in May. Besides a number of small faults several more serious breakdowns occured. The recorder scribing system twice caused trouble, once due to an ink delivery failure, and secondly when the recorder paper jammed. Of more serious consequence was the number of times the Vitron O rings jammed either the syringe or the change over valves, in one or other of the two superspensers. This caused, on two separate occasions, the glass barrels of the syringes to be forced free of their clamps causing serious acid spillage inside the dispensers. The syringe motor was

ruined in one case but in the other spillage little damage resulted. Such an acid spillage is dangerous as a potential electrical fire hazard.

Another irritating failure was the careless breakage of one of the glass heating coils. The replacement coil was unfortunately of a smaller volume capacity. This necessitated a change in the delivery volume of the dispensers to ensure the small air gap did not fill the flow cell. This proved very time wasting to adjust correctly. On reflection it would have been simple to lengthen one of the P.T.F.E. connecting pieces to offset the glass coil volume deficiency.

7.3.6. Very little time due to breakdown occured in June. Time was lost due to the failure of the colorimeter bulb. In addition leakage of air into the system at one of the heating coil connection points, caused air to enter the flow cell and to trigger the safety cut-off device.

7.4. A GENERALISED REVIEW OVER A LONGER OPERATIONAL PERIOD.

During the first 18 months some pattern of performance emerged. There are a great many things which can cause the system to fail. Many trivial things can and have caused time loss or shutdown such as ink and bulb failure, air leakage into the coils and recorder chart roll sticking for examples. Most of them are easily rectified yet cause loss of performance. Some may be overcome by more efficient maintainence, but many are difficult to foresee or forestall.

Of much greater significance are breakdowns due to instrument failure which should be almost eliminated by proper maintainence. Dispenser failure is the most significant

failing. The O rings and gaskets being mostly to blame because of swelling and consequent jamming of either the syringe plunger or change over valve.

The work on the system over an extended period has shown that long trouble free periods are possible with adequate maintainence. Over the longer periods of time some additional faults have occured. Some of the microswitches on the cam timer failed and required replacement, additionally, the fluidised sand bath required overhauling because the steel gauze holding the sand above the heater gradually blocked. It required renewal as did the vanes in the pump supplying the compressed air for fluidization.

7.4.1. Having commented on the mechanical drawbacks of the system it is true to say that the chemistry of the system has performed well. There is still the base line drift but with the regular introduction of a known standard this can be accounted for relatively easily. The standard introduced has been selected to be sufficiently different, from the normal COD. range of the sample, so that there is rarely any difficulty in knowing which recorder trace represents the standards on the recorder chart.

7.4.2. Periodically manual samples are taken of the effluent to coincide with an automated sample, and the sample is analysed as rapidly as possible by the standard manual procedure and the results compared. All automated procedure results have been found to lie within $\pm$ 10 milligrams per litre of the manual result. This is a more realistic way of comparing the agreement between the two procedures, especially when the COD. results are below 100 milligrams per litre level with consequent fall off in

the accuracy of the manual procedure.

Of greater interest in the comparison of the daily average COD. for the automated system, compared with the manual COD. of the daily composite sample, from the automated sampler taking hourly samples. The daily averages for the two procedures often show a larger discrepancy than attributable to experimental error in analysis.

7.4.3. A significant fact to emerge from the experimental results has been the direct relationship of the suspended solids and the COD. results which vary with time in a very close relationship. This was partially to be expected but indicates that the soluble COD. does not vary with time as much as could be expected. This however takes into account only relatively short time periods when the filter beds would not normally show much variation in activity. The soluble COD. would be expected to vary much more over much longer periods of time but would be expected to show only a slow change. As yet there is insufficient evidence on filtered samples analysed in the laboratory to support or disprove what is purely a surmise.

7.5. THE LABORATORY BASED AUTOMATED COD. SYSTEM FOR ANALYSIS OF DISCRETE SAMPLES.

The system designed for the purpose of analysing discrete samples was completed shortly after the re-installation of the monitoring system at Minworth. The two systems are basically similar and deliberately set out and wired the same. Because of the possibility of further systems being required it is an advantage to have replaceable or inter-changeable items common to all systems, especially dispensers.

The system was mainly intended for the analysis of settled

trade effluent samples and the cycle period was set at 5 minutes, giving a 20 minutes heating period for each sample, at a temperature of 160°C. Because of the absence of settleable solids, the homogenising step was omitted from the system. This enabled the use of a turntable top capable of holding 85 of the small 2.5 millilitre polystyrene sample cups. The homogeniser system previously described required the use of a different turntable top capable of holding only 24 of the required 25 ml. cups. The increase is an advantage when longer unattended analytical runs are required.

7.5.1. The system was completed and first used in March 1971. The trial runs were successful once the inevitable minor adjustments on volume settings and lengths of interconnecting tubing had been correctly adjusted. Other minor faults also appeared, such as incorrect timing of cams which require more precision to set than the on-stream system because of the telescoping of the timing sequence.

As the system is mainly under supervision while operating, it is relatively easy to spot and diagnose any malfunctioning of the system and to carry out the necessary repairs. The analytical sequence used also helps to indicate any malfunctioning by including one distilled water sample and one standard after every tenth sample.

The water blank re-established the baseline and indicates the extent of baseline drift, if any, while the reproducability of the peak height of the standard indicates if the system is functioning correctly. Before commencement of the daily analytical run the operator runs water samples to establish the required base line on the recorder graph.

Next 250 milligrams per litre COD. standards are run and the peak height is adjusted by means of the colorimeter range expansion to approximately 90% of the recorder chart width. Then distilled water and standards equivalent to 50, 150 and 250 milligrams per litre COD. are run in duplicate to establish a calibration graph of peak height as COD. value. This calibration graph is subsequently used to determine the COD. value of the samples under test from their peak height.

7.6. SUBSEQUENT MODIFICATIONS TO THE LABORATORY BASED COD. ANALYSER AND THE ANALYTICAL PROCEDURE.

In the light of experience various modifications have been made to simplify and improve COD. analysis. Where applicable and thought to be of benefit, the modification has also been incorporated in the on-stream system.

7.6.1. The initial change involved no equipment modification but rather a change in analytical procedure. Chloride is known to give a direct enhancement of the COD. value of a sample. It also produced a heavy precipitate when mixed with the digestion solution. It soon became clear that high chloride, hypochlorite or chlorine contents were more prevalent amongst the trade effluents than was foreseen. Based on the number of times blockage of the heating coils, flowcell or tubing occured. The danger was that enhanced COD. results could escape detection during routine analysis of a heavy work load, which would be unfair to the trader paying the treatment charge.

As chloride or hypochlorite was found to occur in widely varying sample sources it became essential to screen every trade effluent received, before analysis. This was done by taking

approximately 2 ml. of the settled sample and adding approximately 0.5 ml. of a 2.5% w/v silver nitrate solution in 10% v/v nitric acid. If a precipitate was given, heavier than that given by a 2,000 milligrams per litre standard chloride solution, a chloride removal step was carried out. If the COD. was known by experience to be high the test may be repeated on the sample after some suitable dilution, to see if chloride removal is still necessary. The removal of chloride simply involves mixing the sample and the silver nitrate test solution in equal proportions, and centrifuging to separate the precipitate. The supernatant liquor in the centrifuge tube in retested by addition of one drop of the preciptant to ensure sufficient chloride removal. With excessive levels of chloride present a 10% w/v silver nitrate precipitant is used. Should even this prove inadequate for the complete removal, as has happened in some exceptional cases, no attempt is made to obtain a COD. figure on the sample. Instead an Organic Carbon Value is sought.

It is realised that the precipitate need not be due to chloride, but in most cases it probably is and it would be too time consuming to investigate every individual sample. Chloride removal by precipitation is to be viewed with mixed feelings. It is a retrograde step in possibly lowering the true COD. value by the precipitation or co-precipitation of some organic entity, or by the absorbance of detergent or oil content by the flocculent precipitate. On the other hand it prevents possible penalising of the trader as well as avoiding break down of the analyzer due to blockage.

7.6.2. The standard superspenser units purchased possess driver motors operating at 12 revolutions per minute (R.P.M.). This

allowed the intake/ejection cycle to be completed in 5 seconds, which was an acceptable speed for a repeating dosing syringe, which was its original concept. The high viscosity of the solutions handled created high vacuum conditions on the intake stroke which the O ring seals found difficult to maintain. A longer intake/ejection cycle would, it was thought, reduce the amount of vacuum by applying it over a longer period. Because of the long periods between successive operation of these dispensers slower motors could be easily accommodated. Therefore the existing motors were replaced with 3 R.P.M. motors and subsequent syringes were purchased with 3 R.P.M. motors specified.

These motors seem to have eased the problem of high vacuum. It would probably be even better to use still slowerspeeds of the order of 1 revolution every 3 or 4 minutes for the laboratory system,and even slower speed motors for the monitoring system.

7.6.3. The difficulty which arose with the on-stream monitoring system in always getting the same segment of the solution into the flow cell arose also with the laboratory system. In this case, however, the problem occured more frequently due to having two sets of coils instead of only one set.

The cause of the trouble is the variation in the amount of air taken up after all the mixed solution has been sucked from the mixing pot. The air forms an air gap between successive mixed samples to reduce cross contamination. This air gap needed to vary only slightly to cause trouble to build up. A procedure was devised to regularise the size of the air gap while allowing for slight difference in the

volumes of the two sets of coils. Normally there was suction of all the solution in the mixing pot into the heating coils by the superspenser (C). Figure B. The take-off volume of this superspenser was made equal to the volume dispensed by the superspenser (B). which meters out the digestion mixture. This means there is a residual amount of mixed solution left in the mixing pot, after suction into the heating coils, equivalent to the combined volume of sample and mercury (II) sulphate dilution solution.

The excess solution is removed by suction into a waste bottle before the addition of the next sample and reagents to the mixing pot starts. A small, continuously running, electric blower motor is used with the system to supply air for mixing, to the mixing pot, and to the T joint at the end of the sampling probe for sample agitation purposes. The air intake port of this motor was used to provide suction, via a waste bottle, to a motorised two way valve. The valve is normally open to atmosphere, but on change over the suction is applied, via a short piece of P.T.F.E. tubing, to the mixing pot. The valve is operated by the cam timer which is adjusted to allow sufficient time for removal of excess solution before re-opening the suction to atmosphere. To create the necessary air gap a glass cactus piece with one inlet and three equal outlets is used. The inlet is connected by a short length of P.T.F.E. tubing, equivalent in volume to the desired air gap, which reaches to the bottom of the mixing pot. The centre outlet connects to the waste suction and the other outlets connect to one or other of the two sets of heating coils. The P.T.F.E. tubing which reaches into the mixing pot acts as a common inlet to all three outlets, and is left empty

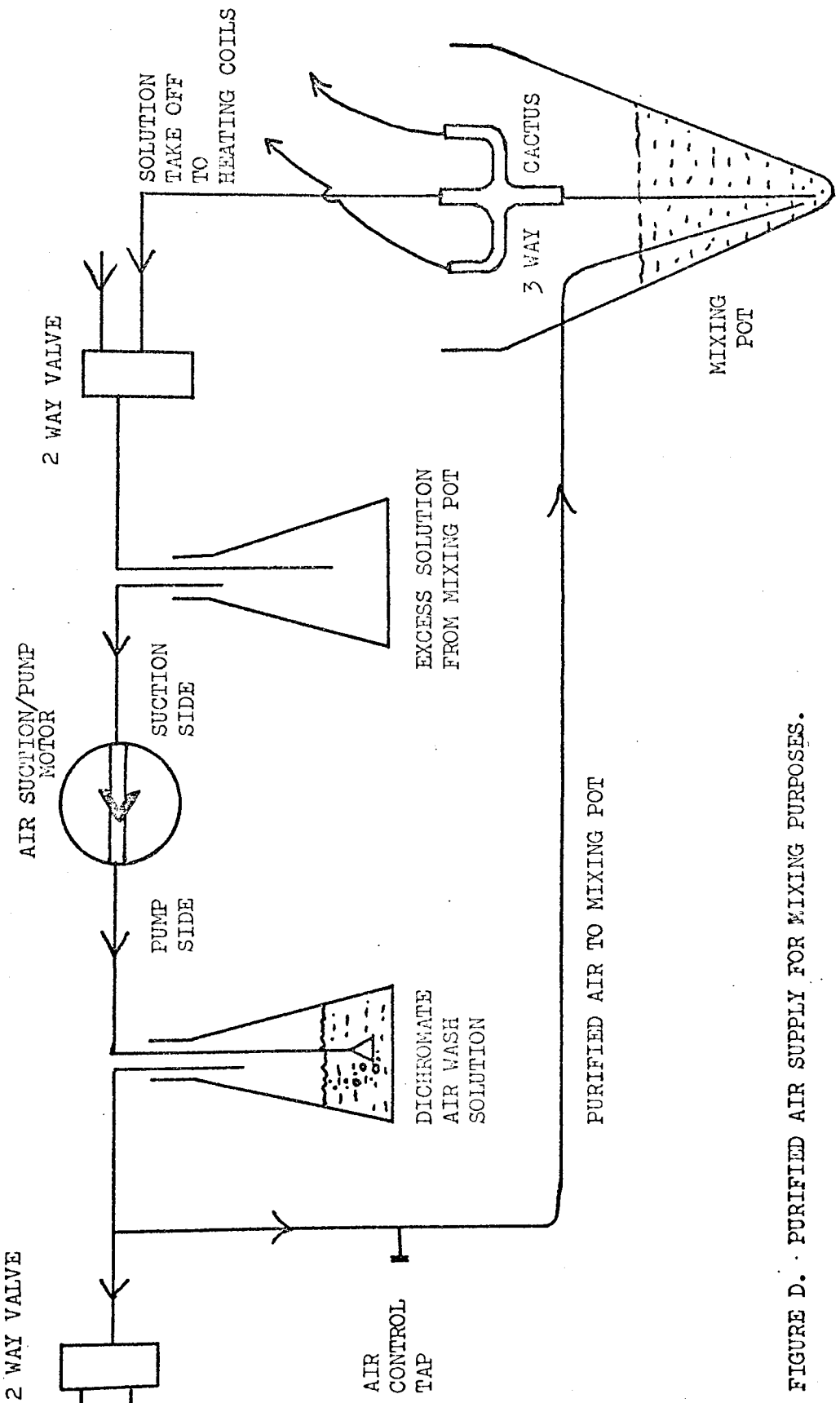


FIGURE D. · PURIFIED AIR SUPPLY FOR MIXING PURPOSES.

after take off of the excess liquor. When suction is applied to take up the next solution into the heating coils, the air in the empty common inlet enters first as the air gap. The air gap is, therefore, always equal and easily adjustable in size. Diagram D. shows the system layout. The procedure has also been included in the on-stream monitory system, using a cactus with 1 inlet and 2 outlets.

7.6.4. The period of blowing air into the sample cups via the sample probe to induce mixing has been curtailed to about 5 seconds. Previously sample mixing by aeration lasted about two minutes, but it was discovered that loss of volatiles during aeration was taking place with some trade effluent samples. Simple alteration of the appropriate timing cam was all that was required.

7.6.5. The fragility of the glass coils have caused a certain amount of trouble. They are perfectly safe in the fluidised sand bath but very vulnerable out of the bath. They require periodic removal to clear the very occasional blockage, but mostly to renew the fluorinated rubber tubing used for interconnection of the various parts of the system. The fluorinated rubber ages gradually in the heating bath losing elasticity and the ability to seal completely. This allows air to leak into the coils. Coil breakage has become quite common during replacement of the rubber seals. This is unfortunate because the coils were specially made and difficult to replace.

One attractive alternative to glass coils was the use of a continuous length of flexible P.T.F.E. tubing stretching from the mixing pot to the flow cell, and being wound in the middle

onto a suitable former to form one long heating coil. The required adjustment in tubing length would be a simple matter. The low cost of the tubing would allow replacement as often as required simply by replacing with a similar length of tubing from the same coil. Trials using the P.T.F.E. tubing coils proved disappointing, giving only about 60% of the oxidation found for benzene and toluene using glass coils. Heating did not appear to be the problem because the P.T.F.E. tubing is very thin walled. It appears as if glass has a hetrogeneous catalytic effect, not exerted by the P.T.F.E., on the oxidation. This is, however, merely conjecture.

7.7. COMPARISON OF ANALYTICAL RESULTS FOR TRADE EFFLUENT SAMPLES.

It is easy to compare the oxidation values given by the manual and automated procedures for any selected set of trade effluents. These results cannot possibly predict the relationship that will exist with every trade effluent analysed, which often vary from sample to sample from the same source.

All that is possible is to test a large number of samples initially, to see if the agreement is acceptable, and to monitor some of the samples, during routine analysis of samples, by both procedures. A routine comparison system has been in operation since May 1972. Each day four to six trade effluents samples are selected from the samples which require to be repeated by the manual procedure, because of their high COD. value. The samples are diluted to bring them into the 100 to 250 milligrams per litre COD. range and this diluted solution is analysed by both the manual and the automated procedure.

7.7.1. Tables 27,28 gives the results found in milligrams per litre COD. for a random cross section of the samples selected. The table lists the trade effluent number and date of sampling, the name of the trader is not included. The COD. result reported is that found for the diluted sample. The dilution figure refers to the number of parts of distilled water mixed with one part of settled sample. The appearance of the settled sample before dilution is also recorded. It is frequently found that samples inneed of dilution are either turbid, emulsified, have a floating oil layer or contain light floating solids. It is not usual to find the selected samples as a single clear liquor, which is of importance when trying to establish the extent of agreement. In most cases the table also indicates the type of effluent or the industrial activity carried out by the trader.

Table 27 covers the period up to the 9th June 1972. The results since the 12th June 1972 are recorded in table 28. on which date the sample aeration for mixing purposes was reduced as stated in paragraph 7.6.4. Some of the poor agreements shown in table 27. are probably due to loss of volatiles during aeration. For example sample 19107 of the 12th June 1972 had a COD. value of 260 milligrams per litre with the reduced aeration, and a value of less than 100 milligrams per litre after the extended aeration used previously.

7.7.2. There are a number of facts bearing on the results shown in tables 27. and 28. also a number of conclusions to be drawn from the results.

(i) The majority of trade effluents give a clear supernatant layer on standing but most of these have COD. values of

TABLE 27

COMPARISON OF MANUAL AND AUTOMATED COD VALUES ON TRADE EFFLUENTS WITH HIGH COD VALUES

DATE	SAMPLE No.	TRADE TYPE CLASSIFICATION	APPEARANCE	DILUTION	COD IN MILLIGRAMS PER LITRE	
					MANUAL PROCEDURE	AUTOMATED PROCEDURE
15-5-72	17119	Steel Fabrication		2	145	145
16-5-72	17808			10	140	115
16-5-72	17031			10	320	230
17-5-72	17952	Brewery		5	220	225
	17979	Vehicle Wash		10	135	130
19-5-72	17650			5	245	265
	18107			50	310	215
22-5-72	17662			5	220	170
22-5-72	18002			20	185	200
23-5-72	17051			200	190	205
24-5-72	18258	Spray Painting		20	190	205
24-5-72	18218	Processed Meat	Emulsion	20	145	125
25-5-72	18239		Emulsion	10	195	150
25-5-72	18190	Bakery	Turbid	10	215	185
26-5-72	16391		Clear, Brown	10	240	240
26-5-72	16395	Soft Drinks	Clear, Yellow	200	145	150
1-6-72	18613	Bakery	Clear	100	205	210
5-6-72	18559	Slaughterhouse	Emulsion	100	200	175
6-6-72	18595		Turbid, Yellow	10	135	150
7-6-72	18913		Emulsion	10	185	165
7-6-72	18599		Oil Layer	50	185	130
9-6-72	18702		Emulsion	50	185	120

TABLE 28

EXTENSION ON THE COMPARISON FROM TABLE 27 AFTER INTRODUCTION OF REDUCED PRE-AERATION

DATE	SAMPLE No.	TRADE TYPE CLASSIFICATION	APPEARANCE	DILUTION	COD IN MILLIGRAMS PER LITRE	
					MANUAL PROCEDURE	AUTOMATED PROCEDURE
12-6-72	19107		Emulsion	10	250; 265	245; 260
12-6-72	19137	Proccessed Meat	Emulsion	10	145	150
14-6-72	18760		Very Turbid	10	230	240
19-6-72	19042	Garage	Turbid	5	265	250
20-6-72	19708	Car Manufacture	Turbid, Oil Layer	10	305	255
21-6-72	17139	Chemicals	Clear	50	160	140
22-6-72	19374	Car Factory	Emulsion	5	250	235
23-6-72	19302	Confectionery	Turbid	10	145	135
26-6-72	19514	Diecasting	Emulsion	100	245	245
27-6-72	17282	Brewery		5	155	160
29-6-72	19377	Spray Paint	Emulsified Paint	100	130	110
30-6-72	19883		Emulsion	20	130	145
3-7-72	17601	Garage	Emulsion, Oil Layer	10	195	130
3-7-72	17604	Plastics	Emulsion, Oil Layer	10	150	170
4-7-72	17323		Turbid, Light Solids	20	120	145
4-7-72	17609	Bakery	Emulsion	20	290	300
5-7-72	19929	Diecasting	Grey Emulsion	5	215; 125	105; 110
5-7-72	19905		Yellow Emulsion	50	230; 265	215; 205
6-7-72	19926	Printing	Oily Emulsion	20	205; 200	230; 195
10-7-72	19946	Dairy	Emulsion, Oil Layer	10	135	120
12-7-72	602		Emulsion	5	250	225
13-7-72	544	Car Factory	Thick Emulsion	50	295	270
14-7-72	643	Car Factory	Emulsion, Oil Layer	5	245	145
14-7-72	715		Turbid	10	150	150
17-7-72	17632		Emulsion	50	270	285

TABLE 23 (Continued)

DATE	SAMPLE No.	TRADE TYPE CLASSIFICATION	APPEARANCE	DILUTION	COD IN MILLIGRAMS PER LITRE	
					MANUAL PROCEDURE	AUTOMATED PROCEDURE
18-7-72	734		Light Floating Solids	10	160	160
20-7-72	400	Bakery	Emulsion, Oil Layer	20	310	315
20-7-72	1014		Emulsion, Oil Layer	10	140	135
20-7-72	785	Electric Bulbs	Turbid	10	170	165
26-7-72	1090	Car Factory	Turbid	20	165	155
27-7-72	362	Slaughterhouse	Clear	5	250	130
31-7-72	17930	Drum Cleaning	Turbid	50	180	175
2-8-72	17390	Wheat Washing	Turbid	5	250	235
9-8-72	1803	Bakery	Turbid, Light Solids	2	185	190
11-8-72	1279	Grinding	Turbid, Grey Solids	50	165	145
14-8-72	1614	Spray Painting	Grey Emulsion	20	170	155
15-8-72	1977	Photo Studio	Turbid	5	295	275
16-8-72	2004	Car Factory	Very Turbid	10	265	240
17-8-72	1650	Plating	Clear Blue Solution	10	180	165
21-8-72	212	Chicken Slaughter	Bloody Solution	10	335	335
22-8-72	18112	Resin Waste	Slightly Turbid	100	220	190
25-8-72	17977	Cooling Water	Turbid	10	185	205
1-9-72	17984	Glue Manufacture	Turbid	50	290	295
5-9-72	2499	Cleaning Drill	Clear	50	165	160
6-9-72	2582	Paint Manufacture	Turbid, Yellow	5	200	205
12-9-72	3014	Caustic Wash Solution	Turbid, Brown Solids	5	235	240
13-9-72	2920	Barrel Cleansing	Emulsion	10	155	150
15-9-72	1988	Ink Roller Wash	Turbid	10	160	170
19-9-72	3257	Photo Drills	Clear, Blue	10	155	135
23-9-72	5003	Vehicle Wash	Turbid	5	155	150

less than 70 milligrams per litre. Many of the samples with COD. values in excess of 250 milligrams per litre were of poor physical appearance. Apart from trade effluents arising from industries connected with food and drink, probably the major cause of high COD. values is the presence of oil and grease, both soluble and insoluble. These items lead normally to a turbid or emulsified appearance in the sample or give a separate oil layer.

(ii) Most of the selected samples would, when undiluted, lie outside the range of the automated COD. system and would be analysed by the manual procedure. However, to obtain sufficient samples for comparison purposes, it was often necessary to use samples whose physical characteristics may have an important bearing on some of the results obtained.

(iii) The main conclusion reached was that the automated method tended to give slightly lower results than the manual method. However, this appears to be less than 10% unless the non homogeneous state of the sample causes variability in the sample aliquots.

(iv) Air mixing in the automated method can easily lead to loss of volatiles from the samples. Probably this directly affected some of the results prior to introduction of reduced aeration, but it is impossible to judge the extent.

(v) The use of a colorimetric procedure as an alternative to the titrimetric system seems fully justified on the basis of these results. Samples with any physical colour, capable of having an effect on the COD. result produced

by a colorimetric finish, are easily picked out visually, and are only rarely received.

(vi) The final conclusion is that the automated procedure for analysis of trade effluents, bearing in mind the various points just outlined, has been justified by results so far obtained. Again bearing in mind the points made, it is doubtful if a completely or partly continuous flow system would have been as successful with these particular samples.

Any tendency to error with the discrete automated COD. system is normally in favour of the trader, while the increased accuracy in the low COD. levels is also a useful gain.

CHAPTER 8.

IMPROVEMENTS TO THE MANUAL PROCEDURE TECHNIQUE AND AN EXAMINATION OF THE SELECTED PARAMETERS.

8.1. PROGRESS TOWARDS A UNIVERSAL STANDARD PROCEDURE.

Despite the emergence of automated procedurs for the COD. test the majority of users will employ manual procedures, because the numbers involved will not justify adoption of an automated system. It is desirable that a basic procedure should be universally adopted and that the parameters involved should be subject to further research before being finally adopted.

8.1.1. The COD. has to a large extent evolved in a comparable manner to the BOD. test. The APHA. 'Standard Methods' (7) define a procedure which is largely accepted throughout the world. Acceptance of this procedure is reinforced by the recent adoption of many of its parameters in the new British 'Standard Methods' (9). This differs only in suggesting a scaled down version using volumes one fifth of the volumes used by the American procedure, in line with the version of the method proposed by Jenkins (29).

8.1.2. Following the 'rapid' COD. test proposed by Jeris (28) has come revived interest (86) in a test described as 'Oxygen Demand Index' (O.D.I.) first introduced by Westerhold (87, 88) in 1965. It differs from the American standard procedure by heating the mixture for 10 minutes in a boiling water bath instead of the conventional two hours reflux. A colorimetric determination as also used instead of a titrimetric finish. The test would appear to be of little value but is seriously

suggested as a method of forecasting the BOD. value of a waste water. It is probable that many other modifications on any eventual universal manual procedure will come and soon go. Objectively one of the real values of any test is its wide acceptance, despite possible shortcomings, in a universal form. These shortcomings could lead to adoption of a modified procedure, but this must not occur without wide acceptance of the need and the value to be gained.

8.2. MEASURES TO IMPROVE THE SCALED DOWN COD. PROCEDURE.

The 'Scale' of the test should be considered as it already differs between different procedures. By scale is meant the volumes employed. The American standard procedure uses a ratio of 1 : 1 aqueous to sulphuric acid composed of 50 millilitres of concentrated sulphuric acid added to 50 millilitres of aqueous solution. This consists of 0.1 Normal potassium dichromate solution and sample mixed in a ratio dependant on the COD. strength of the sample. This imparts a certain flexibility on the analysis by using more sample and less dichromate for lower COD. levels. The new British standard procedure has the same 1 : 1 ratio, but uses only 10 ml. of sulphuric acid to 10 ml. of aqueous solution composed of 5 millilitres of 0.125 Normal potassium dichromate and 5 millilitres of sample or diluted sample. The procedure used by the Upper Tame Main Drainage Authority prior to June 1972 was a scaled down procedure using a 1 : 1.2 aqueous to sulphuric acid ratio. Anticipating the adoption of a 1 : 1 ratio by the British Department of the Environment a new procedure was adopted in April, 1972 using the 1 : 1 aqueous to sulphuric acid ratio. However, to improve accuracy

of the previous procedure the new system used 15 millilitres of sulphuric acid, 5 millilitres of 0.125 Normal potassium dichromate solution, and 10 millilitres of sample or diluted sample. Both procedures are described in the appendix.

It does not make any difference to the results what scale is used. Comparative results between large and small scale procedures show excellent agreement. The small scale procedure for a laboratory engaged in regular analysis of large numbers of samples will show large savings both in money and time. However, for a laboratory carrying out non routine analysis or analysis of a very limited number of samples it would seem wiser to use the large scale procedure. This will minimise lack of analytical practice and ensure greater accuracy.

8.2.1. Personal experience shows that the biggest drawback in using a scaled down procedure is that the accuracy in measuring the separate reagents deteriorates, when large numbers of samples were being handled. Of lesser importance was the refluxing and back titration of the remaining potassium dichromate.

Use of a premixed solution of the potassium dichromate with sulphuric acid and silver sulphate substantially increases accuracy and reliability, and saves considerable time by requiring only a single addition. An Exelo double action pippette has proved excellent for this single addition showing a variation for volume dispensed of less than 0.2%. There is a volume reduction on mixing aqueous solution with sulphuric acid which must be allowed for when adding a premixed solution. For example instead of adding 5 ml. of potassium

dichromate and 15 ml. of sulphuric acid separately to 10 ml. of sample, 18.5 ml. of mixed solution is added and not 20 ml. because of the volume reduction. It is not necessary that the aliquot should contain potassium dichromate equivalent to exactly 5 ml. of 0.125N potassium dichromate. The exact amount of potassium dichromate consumed in the test is measured by the back titration of sample and blanks with accurately standardised 0.125 Normal iron (II) ammonium sulphate.

8.2.2. Increased accuracy for multiple titrations has been found employing semi automated burettes. The analyst uses a simple hand held thumb press switch to control titrant addition. The titrant added being digitably displayed. The titration unit automatically re-zero's on refilling and high accuracy to one hundreth of a millilitre can be achieved.

8.2.3. Uneven and overvigorous heating of the samples often occurs using electric heating mantles, electric hotplates and bunsen burners for refluxing purposes. This must be avoided as it produces poor results and especially variable blanks. Using a gas hotplate consisting of a 15 millimetre top plate heated by an array of gas jets, or alternatively using sand trays, was found to give smooth even heating.

8.2.4. TeKippe et al. (89) recommend and describe the use of air cooled condensers in place of the usual water cooled condensers used in the manual procedure. They claim such condensers are easier to use and are more economical.

8.2.5. The use of colorimetry would appear to be an excellent alternative to the standard titrimetric procedure presently used in the manual procedure. It is a very rapid, highly

sensitive technique which requires no additional reagents, and which requires less analytical expertise than titrimetry. It is also relatively easy to automate where numbers warrant the cost which should be much lower than automated titrimetry.

Gaudy et al. (90). has reviewed the findings of a number of different workers advocating the use of colorimetric measurements for the COD. test. Different workers have used different wavelengths for the purpose, the most common being 440, 600 and 650 nanometres. All are claimed to have been successful for the purpose. Gaudy used a wavelength of 600 nanometres in a fairly extensive examination of colorimetry as an alternative to titrimetry and reported excellent correlation. Most automated COD. systems employ a wavelength of 440 nanometres.

The extended comparison tests between the manual procedure, using titrimetry, and the automated procedure, using colorimetry, outlined in paragraph 7.7, gives a long term indication that there is good correlation for a wide spectrum of samples. One advantage of colorimetry is that the sample is still available for titrimetric analysis, should there be doubt as to the result found colorimetrically, or for use as an occasional routine check.

An automated colorimetric system with associated print-out, capable of processing more than 100 samples per hour, is being actively considered to optimise manual COD. analysis.

8.3. THE CHOICE OF PARAMETERS AND OTHER INFLUENTIAL FACTORS.

As previously pointed out the Americal procedure is largely based on the method proposed by Moore et al. (55, 64), which unwittingly closely resembled the method developed by Muers (68).

The choice of the parameters of temperature, heating periods,

acid concentrations and silver catalyst concentration, seem from the data published to have been chosen rather arbitarily.

8.3.1. The choice of a 1 : 1 aqueous to sulphuric acid volume ratio appears to have been made without much effort to investigate the suitability of other ratios. The ratio used directly controls the reflux temperature and hence the severity of the oxidation. Both Muers and Moore et al. seem to have concluded that the 1 : 1 ratio gave the most severe conditions possible without excessive dichromate decomposition over periods extending up to several hours.

Table 29. shows the extent of potassium dichromate decomposition for various ratios of aqueous solutions to sulphuric acid. The table included the theoretical percentage on a volume basis of sulphuric acid, the reflux temperature of the mixture and the amount of dichromate decomposition, using different reflux periods. This amount of decomposition is given as both actual amount in millilitres of 0.125 Normal potassium dichromate consumed, and also as a percentage of the volume originally present. The tests were carried out by mixing 5 millilitres of 0.125 Normal potassium dichromate, 10 millilitres of distilled water, the appropriate volume of concentrated sulphuric acid, 0.2 grams of silver sulphate and refluxing the mixture for the period stated.

The table shows there is an increase in dichromate decomposition with increasing time and acid concentration, which parallels increasing reflux temperature. Acid concentrations in excess of about 55% v/v produce decomposition which is higher than acceptable over extended heating periods. This is based on a personal opinion that the maximum acceptable

TABLE 29

THE BEHAVIOUR OF VARYING THE ACID : AQUEOUS SOLUTION RATIOS

VOLUME OF AQUEOUS SOLUTION (ml)	VOLUME OF H_2SO_4 (ml.)	RATIO OF AQUEOUS SOLUTION : H_2SO_4	% v/v OF H_2SO_4	REFLUX TEMPERATURE (°C)	REFLUX PERIOD (HOURS)	DECOMPOSITION OF DICHROMATE	
						ml. OF 0.12N SOLUTION	% OF VOLUME ORIGINALLY PRESENT
15	15	1:1	50.0	148	0.5	0.03	0.6
					1.0	0.05	1.0
					2.0	0.10	2.0
					3.0	0.12	2.4
15	18	1:1.2	54.4	159	0.5	0.03	0.6
					1.0	0.14	2.8
					2.0	0.24	4.8
15	21	1:1.4	58.5	168	0.5	0.15	3.0
					1.0	0.3	6.0
					2.0	0.5	10.0
					3.0	0.9	18.0
15	24	1:1.6	61.5	177	0.5	0.25	5.0
					1.0	0.5	10.0
					2.0	0.8	16.0

TABLE 22 (Continued)

VOLUME OF AQUEOUS SOLUTION (ml)	VOLUME OF H_2SO_4 (ml.)	RATIO OF AQUEOUS SOLUTION : H_2SO_4	% v/v OF H_2SO_4	REFLUX TEMPERATURE (°C)	REFLUX PERIOD (HOURS)	DECOMPOSITION OF DICHROMATE	
						ml. OF 0.125N SOLUTION	% OF VOLATILE ORIGINALLY PRESENT
15	27	1:1.8	64.2	184	0.5 1.0 2.0	0.45 0.85 1.5	9.0 17.0 30.0
15	30	1:2.0	66.7	190	0.5 1.0 2.0	0.25 1.1 2.3	5.0 22.0 46.0
15	35	1:2.2	70.0	200	0.5 1.0 2.0	0.50 2.0 3.5	10.0 40.0 70.0

decomposition level is 0.3 millilitres or 6%. Therefore it would on first sight appear that a 2 hour refluxing period using 50% v/v sulphuric acid would prove a good choice.

8.3.2. When the matter of the refluxing period is considered together with the refluxing temperature, the acid concentration/refluxing period combination chosen may not prove to have been the wisest choice.

Two hours is a lengthy reflux time and using 30 minutes or one hour would prove advantageous both for the speed of analysis and the numbers that can be processed. Table 29. shows that the higher boiling points given by increasing the acid concentration give acceptable levels of dichromate decomposition using shorter reflux periods. Temperature is probably a more influential parameter than reflux time. When considering the severity of the oxidation, it is possible that higher reflux temperatures over shorter periods would have proved more suitable than the chosen parameters. This conclusion is supported by examining the results previously quoted using different temperature/time ratios with the automated system, and comparing them with the manual method results. Criticism has been made of the failure of the COD. test when analysing samples which have been subject to tertiary treatment. The degree of purification achieved as seen by reduction in the organic carbon value, for such things as passage through activated carbon, is not often borne out by COD. analysis of the same influent and effluent. It has been suggested that the organic carbon present in the influent is resistant to oxidation and its removal, in some tertiary treatment, is not marked by reduction in the COD. of the effluent. This could

indeed be the case and therefore, more severe oxidation could be required. It may equally be true that the carbon is already in an advanced state of oxidation and would exert only a minimal COD. Therefore, removal of organic carbon would not show a corresponding oxygen demand removal.

8.3.3. An attempt has been made to test the extent of oxidation using various time and temperature combinations with difficult to oxidise compounds. Benzene and pyridine were chosen as the test compounds because benzene is only partially oxidisable, while pyridine is almost completely unoxidisable with the standard COD. procedure. Solutions of known COD. value were prepared from the pure compounds by dissolving in distilled water. The theoretical COD. strength being checked by determining the organic carbon value of both solutions.

The samples were analysed by various modifications of the COD. system. Simultaneously a distilled water blank was determined for each particular modification. The percentage oxidation found based on the theoretical COD. value of the sample could then be estimated. Tables 30 and 31 show the oxidation conditions and percentage oxidations found.

The procedure was to take 5 mls. of 0.125 Normal dichromate solution, add 10 mls. of sample or distilled water and 0.20 grams of silver sulphate. Varying volumes of sulphuric acid, to produce different reflux temperature, were added and the mixed solution was refluxed for a fixed period. The blank values quoted represent the reduction in millilitres of 0.125 Normal dichromate due to decomposition during refluxing of the distilled water blank. The percentage oxidation figures are based on these blank values.

TABLE 30

THE DEGREE OF OXIDATION FOR BENZENE FOUND USING DIFFERENT TEMPERATURE/TIME FACTORS

AQUEOUS SOLUTION (ml)	SULPHURIC ACID (ml)	RATIO OF AQUEOUS TO ACID SOLUTION	REFLUX PERIOD (HOURS)	THEORETICAL COD VALUE OF SAMPLE IN MILLIGRAMS PER LITRE	EXPERIMENTAL COD OF SAMPLE IN MILLIGRAMS PER LITRE	APPROXIMATE % OXIDATION
15	15	1:1	0.5	300	210	70
15	15	1:1	1.0	300	210	70
15	15	1:1	2.0	300	240	80
15	21	1:1.4	0.5	300	270	90
15	21	1:1.4	1.0	300	210	70
15	21	1:1.4	2.0	300	210	70
15	21	1:1.4	3.0	300	195	65
15	27	1:1.8	0.5	300	240	80
15	27	1:1.8	1.0	300	180	60
15	27	1:1.8	2.0	300	150	50
15	27	1:1.8	3.0	300	120	40
15	30	1:2	0.5	300	255	85
15	30	1:2	1.0	300	210	70
15	30	1:2	2.0	300	75	25

TABLE 31

THE DEGREE OF OXIDATION FOR PYRIDINE FOUND USING DIFFERENT TEMPERATURE/TIME FACTORS

AQUEOUS SOLUTION (ml)	SULPHURIC ACID (ml)	RATIO OF AQUEOUS TO ACID SOLUTION	REFLUX PERIOD (HOURS)	THEORETICAL COD VALUE OF THE SAMPLE MILLIGRAMS PER LITRE	EXPERIMENTAL COD OF THE SAMPLE MILLIGRAMS PER LITRE	APPROXIMATE % OXIDATION
15	15	1:1	1.0	400	30	7.5
15	15	1:1	2.0	400	60	15.0
15	15	1:1	3.0	400	100	25.0
15	21	1:1.4	1.0	400	80	20.0
15	21	1:1.4	2.0	400	120	30.0
15	21	1:1.4	3.0	400	160	40.0
15	24	1:1.6	1.0	400	120	30.0
15	24	1:1.6	2.0	400	160	40.0
15	24	1:1.6	3.0	400	160	40.0
15	27	1:1.8	1.0	400	140	35.0
15	27	1:1.8	2.0	400	80	20.0
15	30	1:2	1.0	400	120	30.0
15	30	1:2	2.0	400	120	30.0

The results shown proved rather haphazard and inconsistant. This it is felt was largely the fault of the sulphuric acid. This gave very inconsistant blank figures for the higher percentage acid mixtures when using different acid sources.

The two main conclusions reached were firstly that pre-treatment of the sulphuric acid, probably by boiling, before use would be necessary for high acid concentration using heating periods in excess of one hour. The second conclusion is that greater oxidation over a shorter period of heating is possible by the use of a stronger sulphuric acid concentration.

There is an indication that using an acid concentration of the order of 60 to 65% v/v, giving a temperature range of 170 to 185°C, would give higher oxidations in less than one hour than the present standard methods.

8.3.4. Silver sulphate has proved very effective in catalysing the oxidation of previously difficult to oxidise compounds. In particular the oxidation of short chain aliphatic acids and alcohols.

What seems rather startling is the amount of the reagent recommended for the test. The recommended concentration is 5,000 milligrams per litre in the final mixed solution to be refluxed. The COD. level present in the mixed solution cannot exceed 1,000 milligrams per litre without exhausting the dichromate present. This appears to be a huge excess for a reagent present only as a catalyst. It is possible that chloride in the sample could immobilise the catalytic action of the silver, although addition of mercury (II)

sulphate should effectively complex the chloride and prevent catalyst poisoning.

Replicate samples of a solution of acetic acid were analysed, with varying quantities of silver sulphate present, by the normal manual procedure. The experiment was repeated with the addition of a quantity of chloride and also sufficient mercury (II) sulphate to complex the added chloride. From the results shown in Table 32. it would appear that considerably less silver is required than the quantity specified in the standard methods. Also chloride if complexed by mercury will not impair the efficiency of silver as a catalyst.

However what Table 32. does not show is that the speed of oxidation slows drastically when the silver concentration is reduced. It is easy to see from the colour of a refluxing mixture how far approximately the oxidation has proceeded. It was particularly noticeable that the samples with the normal silver concentration had completed the oxidation in about 30 minutes. The others took much longer and the sample with the lowest silver concentration did not show substantial oxidation even after an hours refluxing. It could be therefore dangerous to advocate a considerable lowering in the level of silver. Palaty et al. (91). found that the greatest degree of oxidation for benzene and acetic acid was by using a mixed silver sulphate/ nickel sulphate catalyst, of 850 and 330 milligrams per litre respectively, in the mixed solution.

8.3.5. Based on results found and their implications, there would seem to be some justification for an extensive review of the

important parameters in the test. This would necessarily need to be sanctioned by an official body for any chance of any major changes recommended being unversally adopted.

TABLE 32

THE CATALYSIS OF ACETIC ACID OXIDATION BY DIFFERENT SILVER CONCENTRATIONS

MILLIGRAMS PER LITRE OF SILVER SULPHATE IN REFLUXED SOLUTION	MILLIGRAMS PER LITRE OF CHLORIDE IN REFLUXED MIXTURE	MILLIGRAMS PER LITRE OF MERCURY(II) IN REFLUXED MIXTURE	THEORETICAL COD OF SAMPLE IN MILLIGRAMS PER LITRE	EXPERIMENTAL COD OF SAMPLE IN MILLIGRAMS PER LITRE	EXTENT OF OXIDATION (%)
5,000	0	0	350	335	96
2,500	0	0	350	315	90
1,250	0	0	350	285	83
500	0	0	350	250	71
0	0	0	350	60	17
5,000	1,000	5,000	350	330	94
2,500	1,000	5,000	350	280	80
1,250	1,000	5,000	350	240	69
500	1,000	5,000	350	210	60
0	1,000	5,000	350	30	8.5

CHAPTER 9.

CONCLUSIONS

Oxygen demand tests are of value in the measurement of water pollution for detection, prevention and treatment purposes. The various forms of test have been briefly surveyed and discussed mainly in comparison to the COD. test. The main emphasis has been on the COD. test. In particular the work involved in developing and testing an automated system for the measurement of COD. values.

9.1. GENERAL CONCLUSIONS

Among the oxidation demand tests it now appears logical to include a chemical as well as biological demand test. A widely held opinion is that a dichromate test would be the most suitable choice. It has been established as a recommended procedure in a number of countries for some time which is a distinct advantage for establishing the test universally. However, from the number of alternative procedures which have been published periodically and from personal observations, the recommended test procedure could benefit from some intensive investigation. It could well be that the investigators would be perfectly satisfied with the present system and not recommend any modifications. It would at least satisfy the advocates of change that the alternatives have been examined.

The ability to automate chemical oxidation demand tests is a big advantage. That there is a desire or a demand for an automated procedure is borne out by the appearance of a number of commercial systems designed to give COD. values of aqueous samples. Some are automated versions of the manual wet oxidation procedure. Others use combustion procedures claiming to give

COD. results equivalent to the manual wet oxidation procedure, and which will give very rapid results. In a recent pollution control newsletter an incomplete survey listed seven commercially available automated COD. analysis systems.(92) The system described in the previous chapters is not commercially available, and is not included in this list.

Automated COD. systems are of potential use for monitoring purposes where there could be a demand not only for conventional or pilot scale sewage works, but also for industrial concerns discharging effluents which must comply with consent conditions as to the oxygen demand content. Automated systems can also be of great use for routine analysis of discrete samples for a busy laboratory. For example automated analysis has been used for many other waste water parameters such as ammoniacal and oxidised nitrogen, anionic detergents and many more. The automated procedure which has been developed has proved extremely valuable in helping to handle large numbers of trade effluent samples.

Because of the extremely wide variety of trade effluent samples being analysed there has been no attempt to correlate the COD. results of these samples with other oxidation demand tests. Many of the samples would inhibit biochemical action and the organic material in many would resist oxidation by the permanganate value test. The COD. and OCV. values for trade effluents and other waste waters are being collected to see what comparisons can be drawn. This is a long term exercise and sufficient data is not yet available. One fact that has proved rather surprising is the high COD. levels found in many trade effluents which would have been thought low. Much of this oxygen

demand is attributable to soluble cutting oils, emulsified insoluble oil and detergents. It is also worth noting that very good agreement has been found by a number of industrial firms who monitor the COD. values of the samples taken by the drainage authority.

9.2. FUTURE DEVELOPMENT OF THE COD. TEST.

The future of the COD. test would seem to be of expansion both as a manual and as an automated test.

9.2.1. The expansion of the manual method is likely to come with adoption of a universally accepted procedure. This will lead possibly, to the adoption of the procedure either as an alternative or as an addition to the much more widely used BOD. test as an effluent standard. The problems of water pollution are very acute in Holland and the Dutch authorities are setting a country wide standard on effluents to combat the problem. The interesting thing is the application of a COD. standard to all effluents which incorporates a variable factor for different types of industry. (93). The different factors are applied to take into account the treatability of the organic waste, and the extent to which it is biodegradeable. The German authorities also seem to favour a chemical oxidation standard for effluents through rather suprisingly they favour the PV. test. (94). There is no universal trade effluent policy in the United Kingdom with different authorities favouring different systems and in some cases not applying any standards to discharges. However, this could alter with the formation in 1974 of a limited number of Regional Water Authorities responsible for controlling and monitoring all effluents both domestic and industrial.

9.2.2. It is difficult to forcast which way the automation of the

COD. test will proceed. There seems every chance that it will assume greater importance because the sensible thing with any analytical test is to automate it if possible, should the number of samples warrant automation. Similarly monitoring of effluents is developing quite rapidly and the COD. is at least as good as any other measure at present used. What it is difficult to forcast is whether any physical chemical procedure will become acceptable as an alternative to automation of the wet chemical procedure. It is a personal opinion that they could never produce as consistent an agreement with the manual procedure as automated wet chemical methods. In specific cases there could be good enough agreement to allow their usage for monitoring purposes.

9.3. FUTURE DEVELOPEMENTS WITH THE DISCRETE AUTOMATED COD. SYSTEM.

The results from the automated wet chemical system described in this thesis have been sufficiently encouraging for a decision to be taken to build several more systems for both laboratory and monitoring purposes. The opportunity is being taken to modify, not the procedure, but the instruments used in the system. Because of the trouble with the erratic behaviour of the two way valves in the system a simple two way P.T.F.E. tap mechanised by addition of a small electric motor or a pneumatic valve will replace all two way valves. The digestant solution dispenser may be replaced by a version of the Exelo double action pippette automated by fitting a motor on the change over tap. Tantalum, platinum and other metal coils are actively being considered as alternatives to glass. Though expensive the possibility of coil breakage would be removed completely. Tests show that neither tantalum or platinum affect or are affected by the digestion solution.

A combined colorimeter-print out system developed for use with other automated analytical equipment will be used in future systems.

9.3.1. Further simplifications for the monitoring system would always be welcomed. In a situation where conditions alter only slowly and instantaneous monitoring of changes is not required this is possible. In this situation it is sufficient to collect a composite sample over a period of about 30 minutes and then analyse the composite. A discrete system of the type developed by the Axel Johnson Institute, Sweden, would be very suitable for this type of monitoring, if used in a scaled down version. Basically the composite sample would be mixed with the digestion solution in a heating vessel which also acts as the colorimetric cell. The change in optical density with time is monitored using flexible fibre glass optics fitted to the colorimeter, which feeds a signal to a recorder. After the appropriate heating period a valve on the heating vessel is opened allowing the contents to drain to waste. The number of working parts and operations is therefore reduced to a minimum.

Such a system would be of greatest use in long term evaluation or data collection on a large scale discharge where the quality change may be large but slow. Instances are sewage works, very large industrial concerns and rivers.

In all aspects of wastewater measurement and treatment, the measurement of the organic matter by oxidation demand has always played an important role.

The increasing complexity and divergence of waste water technology calls for some broadly applicable, basic reference test for measurement of organic content.

It is suggested that the chemical oxygen demand test (COD.) could fulfill this requirement.

APPENDIX.

1. CHEMICAL OXYGEN DEMAND; SEMI-MICRO PROCEDURE.

The procedure specified for analysis of trade effluents and sewage works samples by the Upper Tame Main Drainage Authority. (This procedure was superceded April 1972).

SUMMARY.

5.0 ml. of sample or diluted sample are refluxed for 2 hours with 5.0 ml. of potassium dichromate and 12.0 ml. of concentrated sulphuric acid. The amount of dichromate consumed in oxidising the sample is measured and from this is computed the COD. value of the sample.

REAGENTS:

1. potassium dichromate 0.125N. Dissolve 6.129 g.A.R. potassium dichromate in distilled water. Dilute to 1 litre.
2. Iron (II) sulphate 0.125N. Dissolve 34.75 g.A.R. $FeSO_4 \cdot 7H_2O$ in 100 ml. of 25% H_2SO_4 V/V. Dilute to 1 litre. This solution must be checked against the dichromate each day before use.
3. Silver sulphate. A.R. Salt.
4. Mercury (II) sulphate. A.R. Salt.
5. Sulphuric acid. A.R. grade S.G. 1.84.
6. Iron (II) - 1:10 phenanthroline indicator. Dissolve 3.475 g $FeSO_4 \cdot 7H_2O$ in 500 ml. of distilled water. Add 7.427 g of 1:10 phenanthroline monohydrate. Shake until dissolved. The indicator is also available from BDH as a ready made reagent solution.
7. Anti-bumping granules.

APPARATUS:

A flat bottomed flask of 150 ml. capacity having a 4" neck and B.19 ground glass socket is fitted with a 12" double surface condenser fitted loosely with a glass cap. A hotplate giving uniform heating is essential.

METHOD:

Chloride ion interference.

No interference occurs with a chloride ion concentration of less than 100 mg/l and Method A is used. Mercuric sulphate is used, as in Method B, to suppress the chloride interference. It is effective up to concentrations of 500 mg/l Cl^-. Only slight interference occurs at concentrations of 1000 mg/l Cl^-.

A. For samples containing not more than 100 mg/l chloride ion.

Add 5 ml. of Reagent 1 and 12 ml. of Reagent 5 to the flask. Cool in a tray containing cold running water. Add 0.2g of Reagent 3, 5 ml. of sample (or an aliquot diluted to 5 ml) and fit to the condenser. Mix, add a few anti-bumping granules and oil gently under reflux for 2 hr. Cool. Add 45 ml. of distilled water and cool in running water until cold. Add 1 spot of Reagent 6 solution and titrate residual dichromate with Reagent 2 from a 5 ml. micro burette.

B. For samples containing more than 100 mg/l chloride ion.

To 5 ml. of sample (or diluted aliquot) add 0.2 g of Reagent 4 and shake thoroughly. Immerse the flask in cold running water. Add 5 ml. of Reagent 1 solution, 12 ml. of Reagent 5 and 0.2 g of Reagent 3. Fit the flask to the condenser and continue the determination as before. Carry out three

blank determinations in a similar manner to the method used, replacing the sample with 5 ml. of distilled water.

CALCULATIONS:

Subtracting the sample titration from the blank titration in ml. of 0.125N iron (II) ammonium sulphate gives the volume of potassium dichromate equivalent to the oxygen demand of the sample. Since 1 ml. of 0.125N potassium dichromate = 1 mg. of oxygen.

Calculate COD from:

$$\text{COD} = \frac{(\text{Blank titration} - \text{sample titration}) \times 1000}{\text{ml of sample taken}} \text{ mg/l}$$

NOTES:

1. Absolute cleanliness is essential in this determination at all times. Protect the flasks from dust by inverted test tubes or glass wool plugs.
2. Do not overheat during refluxing. This can cause erratic results due to breakdown of the dichromate to chromic salts.
3. The average value for many blank determinations on the reagents is equal to approximately 0.3 ml 0.125N. On a 5 ml. sample this is equivalent to a COD. of 60 mg/l. By carrying out determinations in triplicate and with care it is possible to obtain reliable results with titration differences (after making allowance for the blank) of 0.2 ml 0.125N. This is equivalent to a COD. of 40 mg/l on a 5 ml sample. By concentrating liquids to one tenth their colume and taking 5 ml. the minimum COD. that can be determined is approximately 5 mg/l. Tested with good sewage effluent and with tap water, concentration of the liquids did not result in any reduction of the COD.

If the minimum acceptable titration value is taken to be twice the blank value, i.e. 0.6 ml. and the volume of sample taken is 5 ml. then the minimum COD. value of the sample analysed, without concentration, is 60 mg/l. Therefore with samples below 60 mg/l COD. only an indication of the level is given, unless the sample is pre-concentrated.

4. It is permissible to dissolve the silver sulphate (Reagent 3) in the sulphuric acid (Reagent 5) at a concentration of 25 g to a standard 2.5 litre winchester. This obviates separate addition. Care should be taken to ensure complete dissolution of the silver sulphate, which takes several days to complete.

5. Multiple blank values must not vary from a mean average by more than 0.1 ml.

6. Potassium Hydrogen Phthalate can be used as a standard for this determination. 408.44 g of Potassium Hydrogen Phthalate requires 480 g of oxygen for complete oxidation. 0.850 g of analar Potassium Hydrogen Phthalate dissolved in 1 litre of distilled water gives a solution with a theoretical COD. value of 1000 mg/l.

   In practice using this solution diluted to suitable values recoveries of the order of 96% are normally found.

7. Samples in excess of 100 mg/l COD. should duplicate to within 5% although the American Standard methods quotes a standard deviation of $\pm$ 8.2% of the calculated oxygen demand of reagent grade glucose.

PRE-TREATMENT FOR TRADE EFFLUENT SAMPLES.

The COD. value for trade wastes are determined on the samples after settling for a minimum of one hour. A pyrex test tube is completely filled with shaken sample and allowed to settle for a minimum of 1 hour. A 5 ml. sample is taken by a 5 ml. glass syringe, a large bore needle is used and the sample is taken approximately 2 ins. below the surface. This sample aliquot is either used direct or diluted to some required dilution from which 5 ml. aliquots are taken for the analysis.

Samples which do not give a corrected titration i.e. Blank titration - sample titration between 1.0 and 4.0 must be repeated on some more suitable dilution. This however is not possible for samples where a 5 ml. aliquot of the original sample has a titration difference of less than 1 ml.

2. CHEMICAL OXYGEN DEMAND; AMENDED PROCEDURE INTRODUCED APRIL 1972.

The semi-micro procedure for use by all laboratories of the Upper Tame Main Drainage Authority as the approved method of testing all samples.

SUMMARY.

10.0 ml. of sample or diluted sample are refluxed for 2 hours with 5.0 ml. of potassium dichromate and 15.0 ml. concentrated sulphuric acid. The amount of dichromate consumed in oxidising the sample is measured and from it is computed the COD. value of the sample.

MODIFICATION.

The 1 : 1.2 aqueous solution : sulphuric acid ratio of the now superceded semi-micro procedure has been altered to a 1 : 1 ratio in anticipation of the publication in 1972/73 of a new standard British procedure recommending the use of the 1 : 1 ratio specified by the American standard procedure.

The volumes chosen are arbitary. The significant volume is the increase to 10 ml. of the sample volume. This increased the overall accuracy of the semi-micro procedure and lowers the lower limits at which reported results can be accepted with reasonable confidence.

REAGENTS.

1. Potassium dichromate. 0.125N. Dissolve 6.129 g. A.R. potassium dichromate in distilled water. Dilute to 1 litre.

2. Iron (II) ammonium sulphate 0.125N. Dissolve 49.020 g. A.R. $Fe(NH4)_2(SO4)_2\ 6H_2O$. in 100 ml. of 25% v/v sulphuric acid and dilute to 1 litre with distilled water. This

reagent MUST be checked daily against Reagent (1) before use.

3. Mercury (II) sulphate. A.R. grade solid.

4. Silver sulphate. A.R. grade solid.

5. Sulphuric acid. Any reasonable grade may be used. The only criteria is that it should possess a blank value equivalent to no more than 0.3 ml. and preferably less than 0.2 ml. of 0.125N dichromate solution.

6. Iron (II) - 1.10 Phenanthroline indicator. This indicator is available as a ready made reagent from major laboratory supply houses.

PREMIXED DIGESTION SOLUTION.

Into a 5 litre pyrex flask measure 730 ml. of distilled water, 100 ml. of solution containing 53 g. of A.R. potassium dichromate per litre of distilled water and 25 g. of A.R. silver sulphate. Add carefully with frequent swirling 1 winchester (2.5 litres) of sulphuric acid. The mixed solution should be stood overnight and again swirled before use.

NOTES.

(i) The flask should be stood in a sink during the acid addition and overnight while cooling. The operator must wear safety goggles when mixing.

(ii) Any undissolved silver sulphate will dissolve on standing overnight.

(iii) The mixed reagent is stable for long periods, if not subject to active light, by storing in a dark glass bottle or in the dark.

(iv) Because of a volume reduction on premixing, the addition of 18.5 ml. of the solution is equivalent to adding 15 ± 0.2 ml. of concentrated sulphuric acid, 5 ± 0.1 ml. of aqueous solution which is approximately 0.125N with respect to potassium dichromate and 0.15 ± 0.02 g. of silver sulphate.

(v) By adding exactly 18.5 ml. from the same digestion solution to all blanks, standards and samples in the same analytical run all will receive identical amounts of the three reagents with considerably greater speed and accuracy than the separate addition of all three reagents.

(vi) As can be seen from the calculation equation the exact strength of the dichromate is unimportant. The equation relies on the iron (II) ammonium sulphate titrant strength being known exactly.

APPARATUS.

1. An 'Exelo' double action pippette or some similar piece of equipment capable of making additions, of a high standard of reproducibility and accuracy, of the digestion solution.

2. Flat bottomed, short necked round flasks or ehrlermeyer flasks of about 150 ml. capacity fitted with ground glass B.19 joints for refluxing. Any type of single or double surface water cooled condenser fitted with a B.19 socket, and at least 10 inches in length.

3. A gas heated hot plate or heated sand tray both provide even, uniform heating to give reasonably vigorous

refluxing. Uniform heating is essential and it is not found necessary to use boiling aids when the heating is uniform.

4. A 5 ml. micro burrette or a digital display automated titrator. Mixing during titration should be by means of a magnetic stirrer using a P.T.F.E. covered stirring bar.

METHOD.

To 10 ml. of sample or diluted sample add 0.4 g of mercury (II) sulphate and swirl thoroughly. Add 18.5 ml of digestion solution, swirl to mix and fit the flask to a condenser. Reflux for two hours. Allow the flask to cool somewhat, add 50 ml. of water, swirl to mix and cool down in running water until cold. Add 1 or 2 drops of the indicator and titrate the residual dichromate with 0.125N. iron (II) ammonium sulphate.

Run a minimum of 3 blank determinations through the method using 10 ml. aliquots of distilled water in place of the sample.

Additionally run a known strength potassium hydrogen phthalate standard as a method check.

Titration of a blank without refluxing will give the blank value of the sulphuric acid, if this had not been checked prior to its usage, for making up the digestion solution.

CALCULATION:

Since 1 ml. of 0.125N potassium dichromate = 1 mg. of oxygen the amount of potassium consumed in the test is a direct measure of the oxygen demand of the sample.

COD. of the sample = $\frac{A - B}{C} \times 1000$ mg/l.

A = Blank titration in ml. of 0.125 N. iron (II) ammonium sulphate.

B = Sample titration in ml. of 0125N. iron (II) ammonium sulphate.

C = ml. of original sample used in test.

PROCEDURE NOTES.

i. Absolute cleanliness of all equipment is essential. Rinse the inside of condensers after use. Reflux flasks should simply be washed under running tap water, then stored upside down to drain and protect from dust preferably away from laboratory fumes. If unused for more than 3 or 4 days swirl with a small amount of sulphuric acid and tap water then rinse with distilled water before re-use.

ii. Because the blank value will be in the probable range 0.15 to 0.30 ml. any figures quoted below 30 mg/litre COD. are more indicative than accurate and should be regarded as such, and should be sensibly quoted to the nearest ten. i.e. 0, 10, 20, 30 mg/litre.

iii. Potassium hydrogen phthalate is used as a standard reagent 0.850 g. of the pure dry salt dissolved in a litre of distilled water gives a solution with a theoretical COD. value of 1,000 mg/l. In practice recoveries of about 96% are normally found.

iv. Multiple blank values must not vary from the mean average by more than 0.1 ml. The occasional rogue result should not be included in any mean average, any

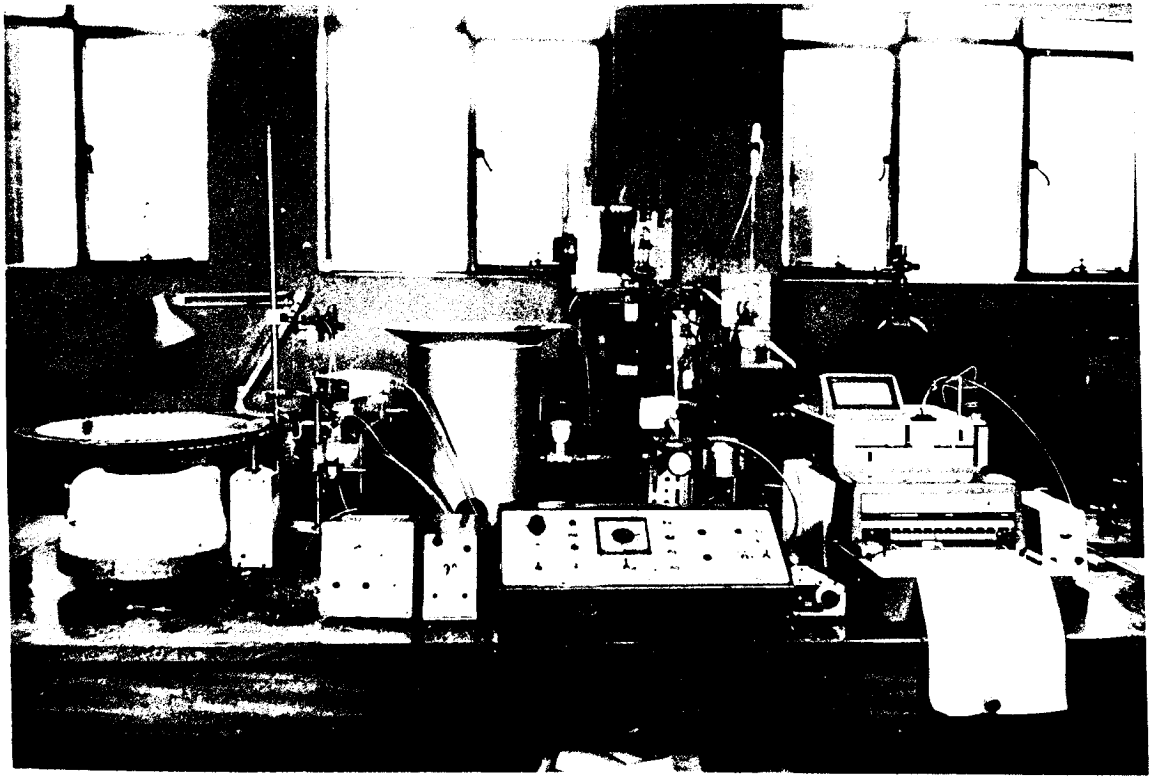
greater frequency in deviation should be treated seriously.

TRADE EFFLUENT SAMPLES.

i. Samples must be settled for a minimum of 1 hour. The sample being taken by syringe direct from the supernatant layer in the sample bottle.

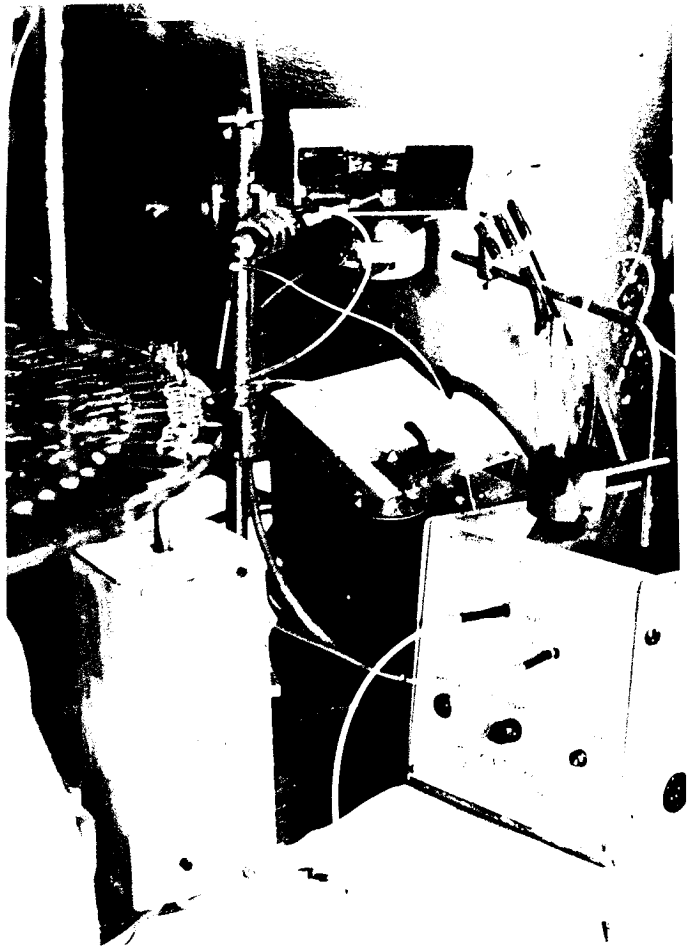
ii. All samples must be checked roughly quantitatively to ensure the chloride level does not grossly exceed 1000 mg/litre. Samples in excess of 1,000 mg/l should be subject to a chloride removal stage.

iii. All samples in excess of 1,000 mg/litre and when possibly 500 mg/litre COD. value must be repeated at a different sample dilution.

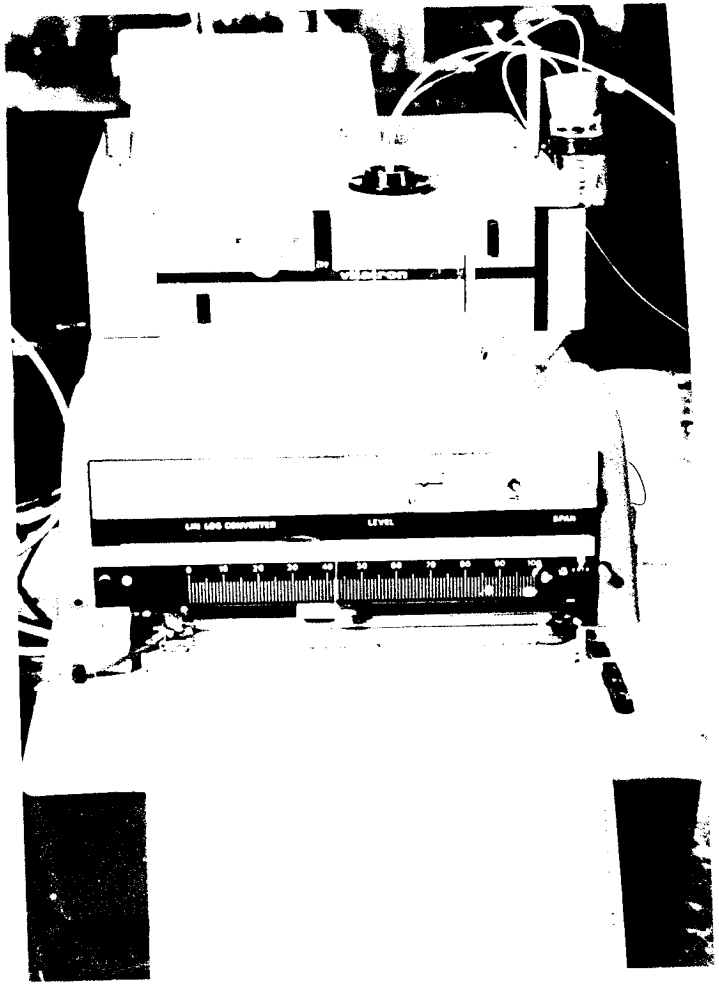


The Discrete Automated COD System.

Photograph 1



Sampling/Mixing/Sand Bath System.



Colorimeter/Recorder System.

Photograph 2

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